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#42635 Summary

Submission

Authors	Akram La Kilo, Alberto Costanzo, Daniele Mazza, Muhamad Abdulkadir Martoprawiro, Bambang Prijamboedi, Ismunandar Ismunandar
Title	Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation
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Submitter	Dr. Akram La Kilo ✉
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Editor	Saprizal Hadisaputra ✉
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Submission Metadata

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Title and Abstract

Title	Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation

Abstract

BIMEVOX had the potential to play an important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, oxide ion migrations of γ-$Bi_2VO_{5.5}$ *and BIMEVOX were simulated using density function theory (DFT), Mott-Littleton method, and molecular dynamic simulation. In γ-*$Bi_2VO_{5.5}$*, there were oxygen vacancies at the equatorial position in the vanadate layers. These vacancies could facilitate oxide ions migration. The Enthalpy of the oxide migration for γ-*$Bi_2VO_{5.5}$ *based on DFT calculation was 0.38 eV, which was in a good agreement with experimental results. The γ-*$Bi_2VO_{5.5}$ *can be stabilized by partial substitution of* V^{5+} *with* Cu^{2+}, Ga^{3+}, *and* Ta^{5+}*. Defect simulation results using the Mott-Littleton method showed that the total maximum energies of region II were achieved at concentrations of 10, 10, and 20%, respectively for* Cu^{2+}, Ga^{3+}, *and* Ta^{5+}*. The calculated concentration of* Cu^{2+}, Ga^{3+}, *and* Ta^{5+} *were in a good agreement with those of experiment results, where the highest ionic conductivity obtained. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-*$Bi_2VO_{5.5}$ *and BIMEVOX (ME = Cu and Ta) respectively were 0.19, 0.21, and 0.10 eV, close to experimental values.*

Indexing

Keywords	simulation; vacancy defect; γ-Bi2VO5.5 and BIMEVOX; ionic migration

Language en

Supporting Agencies

Agencies –

References

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conductivity characteristics of $Bi_4Mg_xV_{2-x}O_{11-\delta}$ ($0 \leqslant x \leqslant 0.3$) as solid electrolyte for intermediate temperature SOFC application, *J. Alloys Compd.*, 589, 29–36.

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#42635 Review

SUMMARY **REVIEW** EDITING

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Authors	Akram La Kilo, Alberto Costanzo, Daniele Mazza, Muhamad Abdulkadir Martoprawiro, Bambang Prijamboedi, Ismunandar Ismunandar ✉
Title	Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation
Section	Articles
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Round 1

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Title	Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation
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Dear Dr. Akram La Kilo,

We have reached a decision regarding your submission to Indonesian Journal of Chemistry, "HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION".

Our decision is: Revisions Required

Comments of the reviewers can be seen in the bottom part of this email.

The revised paper has to be completed with the responses for the reviewer's comments, point by point, in table form at the beginning of the page of the revised paper. It is also required to highlight the revised parts with a different color of letters.

The revised paper has to be resubmitted in the system within three weeks.

Thank you for your intending to contribute to the journal and for giving us to read your work.

Best regards,

Saprizal Hadisaputra
Department of Chemistry Education, Faculty of Science and Education, University of Mataram
rizal@unram.ac.id

Reviewer A:

Additional Comment::

Reviewer B:

Additional Comment::
I have read the manuscript with the title "HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10%

I have read the manuscript with the title "HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION", the work seems to be interesting and looks important.

In my opinion, the manuscript should be masivelly rewritten due to the following reasons:

General
1. Some typographical errors are spotted, like "dopents".
2. Use consistent unit. There are mixing between temperature unit of K and C.
3. The references should follow IJC format.
4. Check the English grammar.

Scientific points
1. The reason to investigate the phase of Bimevox seems to contradict with the reason that bimevox is more efficient than conventional SOFC materials at low temperature. The phase is stable at higher temperature. Why would authors not investigate the lower temperature phases?
2. The experimental works related to the present work are too old. There should be more recent works dealing with bimevox if indeed the materials are useful and technologically applicable.
3. For me, the computational methodologies are a still unclear. The first part of the methods explains the calculations of the activation energy. What kind of activation energy is not explicitly mentioned. Is it oxygen migration activation energy? If so, in my opinion, the term should be changed into oxygen atom/ion migration barrier. I also believe that the authors employed the nudge elastic band method to find the minimum energy pathway. If so, mention it in the text.
4. Still in the same section, I found that many important details are missing. What DFT functional was used in the current work? If the authors employed planewave basis set, mention the kinetic energy cutoff. Also, the k-point sampling method and k-point grid must be mentioned. On the other hand, there are many unecessary details that are mentioned in the text such as "… density functional theory (DFT) that states the total energy of the system of electrons in the external potential is a unique function of the ground state density…" and the like. Such an information is generally known. The section should be rewritten systematically to show the most important details.
5. The BVS method should have some brief theoretical background. Add some relevant equations to clarify the written text. Also, add some more recent "successful" works based on the BVS method if indeed the method is a best method for this kind of work.
6. Add references of the Mott-Littleton method. Also, add some relevant equations of this method if possible.
7. The equation to calculate the defect energy should be mentioned. Example: Malyi, et al Solid State Ionics 212 (2012) 117–122.
8. The experiments were conducted at >500 C. However, the computational methodologies do not mention any temperature. In what temperature were the calculations conducted? What is the effect of

the experimental temperature to the quantitative results of the computational study?
9. Does the Figure 1 show the phase?
10. The y-axis on the Figure 4 should be relative energy, i.e. the lowest energy configuration should be shifted to 0.
11. There should be any figures showing each position of oxygen in addition to the graph of Figure 4.
12. I think the comparison between the theoretical results with the experimental results as listed in table 1 is not a fair comparison. The computational results only calculated the oxygen migration barrier and pathway in Bi4V2O11 (Bivo ?) while the experimental results show the Bimevox materials, i.e. has some metal dopants. I believe that there are significant effects of addition of metal into the structure to the migration barrier (cf. Introduction). If possible also calculate the oxygen migration barrier and pathway of the bimevox.
13. The authors should emphasize the theoretical results to the perspectives towards experiments, i.e. so what if the results are in good agreement with the experiment results? What can the readers learn about the conclusions?

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Dear Editor

Thank you for your very careful review of our paper, and for the comments, corrections and suggestions that ensued. A major revision of the paper has been carried out to take all of them into account. And in the process, we believe the paper has been significantly improved.

Looking forward hearing from you soon.
Sincerely,

Akram La Kilo

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Subject: HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION

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Dear Saprizal Hadisaputra

Thank you for being careful and quick to respond to our manuscript. In addition to the required repairs, we also added two paragraphs to the reason why Ta dopants have high ion conductivity compared to Cu and Ga dopants.

We are waiting for the next good news as progress shall mean for us this manuscript to be published in the IJC.

Best regards,

Akram La Kilo

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Dear Dr. Akram La Kilo:

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Our decision is to: Accept Submission

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Thank you for your valuable contribution to the journal.

Best regards,

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HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION

ABSTRACT

BIMEVOX oxides have potential to play an important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, ionic conductivity of γ-$Bi_4V_2O_{11}$ and its dopents, is simulated using density function theory (DFT), bond valence sum (BVS), and Mott-Littleton method. In γ-$Bi_4V_2O_{11}$, there are oxygen vacancies at the equatorial position in the vanadate layers. These vacancies can facilitate oxide ions migration. The calculated activation energy of the oxide migration for γ-$Bi_4V_2O_{11}$ based on DFT calculation is 0.38 eV, which is in a good agreement with experimental results. Oxygen migration, based on BVS result, mainly occurs in equatorial plane, i.e. on the [140] direction in γ-$Bi_4V_2O_{11}$. The BVS minimum achieved is 1.320, which is considered as a site that has large cavity and facilitate oxygens hopping. The γ-$Bi_4V_2O_{11}$ can be stabilized by partial substitution of V^{5+} with Cu^{2+}, Ga^{3+}, and Ta^{5+}. Defect simulation results using the Mott-Littleton method showed that the total maximum energies of region II are achieved at concentrations of 10, 10, and 20%, respectively for Cu^{2+}, Ga^{3+}, and Ta^{5+}. The calculated concentration of Cu^{2+}, Ga^{3+}, and Ta^{5+} are in a good agreement with those of experiment results, where the highest ionic conductivity obtained.

Keywords: DFT, BVS, defect, γ-$Bi_4V_2O_{11}$ and BIMEVOX.

INTRODUCTION

Solid electrolyte materials with high oxide ion conductivity at low temperature are intensively investigated in order to have solid oxide fuel cell (SOFC) capable of operating at low temperature. One of oxide materials that has high oxide ion conductivity is $Bi_4V_{2-x}Me_xO_{11-\sigma}$ (BIMEVOX) with ME = Ta, Cu, Ga, Ta, etc. As comparison with the materials widely used solid electrolyte material, such as yttria stabilized zirconia (YSZ), BIMEVOX has ionic conductivity of $1x10^{-2}$ Scm^{-1}, which is around three orders of magnitude larger than YSZ at same temperature of 300 °C [1]. Therefore BIMEVOX has potential application as electrolyte in SOFC working at low temperature. BIMEVOX also has potential application as oxygen separation devices and for catalytic inorganic membrane reactors (CIMRs) [2].

BIMEVOX is family of oxides derived from $Bi_4V_2O_{11}$ (BIVOX) and obtained by doping into the vanadium site of $Bi_4V_2O_{11}$ by aliovalent or isovalent metal cations (ME). The structure of $Bi_4V_2O_{11}$ can be derived from Bi_2MoO_6 and δ-Bi_2MoO_6 by formation of oxygen vacancies in the metal oxygen layers; thus the compound can be formulated as $(Bi_2O_2)(VO_{3.5}\square_{0.5})$, where $\square$ is corresponding to the intrinsic oxygen vacancies [3, 4].

The $Bi_4V_2O_{11}$ goes to several structural transformations and known has several polymorphs, but essentially there are only three main polymorphs, namely α, β, and γ-$Bi_4V_2O_{11}$ with the transformations: $\alpha \rightarrow \beta$ at 447 °C and $\beta \rightarrow \gamma$ at 567 °C. The structures of α and β-phases are more ordered, larger in unit cell and have lower conductivity. At the high temperature, γ-phase is formed and has conductivity of 0.2 Scm^{-1} at 670 °C [5]. The γ-$Bi_4V_2O_{11}$ can be stabilized at lower temparature by partial substitution of V^{5+} with other metal cations (ME) [6-10]. The substitution do not only stabilize the structure but also increase ionic conductivity due to the creation of vacancies. Transition metals such as Cu, and Zn can be used to substitute V in γ-$Bi_4V_2O_{11}$ which lead to stabilization of the tetragonal structure and also gives high oxide ion conductivity at intermediate temperature, 500-950 K [11].

Polarizability of dopants in the γ-$Bi_4V_2O_{11}$ plays an important role in the stabilization of the structure as well as to oxide conductivity. For example, the ionic conductivity of $Bi_2Cu_{0.1}V_{0.9}O_{5.5-\delta}$ is higher than $Bi_2Zn_{0.1}V_{0.9}O_{5.5-\delta}$ since the polarizability of Cu^{2+} is larger than Zn^{2+} [12]. Therefore the cation ability to polarize oxygen can also facilitate hopping of oxygen in the structure [8]. Meanwhile, the ionic radius of metal dopans are also important to the conductivity. This mean that the dopant with ionic radius close to the V^{5+} radius could enhance the conductivity [13].

Experimental studies on the oxide ionic conductivity of BIMEVOX has been reported, elsewhere [14]. However, the experimental study could not reveal the detail of the mechanism of oxide ioni conductivity and role of dopant in the BIMEVOX on the structural properties. Computational studies could be used to study many material properties efficiently in order to save time and cost as well as to provide more detail mechanism in the atomic level. Some computation study on the layered structure of Aurivillius phases similar to BIMEVOX has been carried out and reported [15, 16]. It could reveal defect energies and maximum dopant concentrations in Aurivillius as ferroelectric material. From our best knowledge, the computational study on BIMEVOX is not reported yet.

Here, we report the computational study on BIMEVOX and its parent structure that cover trajectory of ionic oxide in γ-$Bi_4V_2O_{11}$ and defect and stability structure of BIMEVOX. The study was aimed to investigate the oxide ion pathways that are possible in the V^{5+} coordination environments of γ-$Bi_4V_2O_{11}$ as well as to predict dopant concentrations of Cu^{2+}, Ga^{3+} and Ta^{5+}

that give the higher ionic conductivity. Those dopants were selected because of its ionic radius close to ionic radius of V^{5+}.

METHODS

Activation Energy

Activation energy is calculated from the minimum enthalpies of various ionic oxide positions in of γ-$Bi_4V_2O_{11}$ structure. The enthalpies are calculated by using computational simulation method that is based on density functional theory (DFT) that states the total energy of the system of electrons in the external potential is a unique function of the ground state density. This simulation used CASTEP code of Material Studio Modeling from Accerys, series number 3.2.00, in Politecnico di Torino [17]. Methodology for electronic structure calculations in CASTEP is as follow: set of one-electron Schrodinger (Kohn-Sham) equations are solved using the plane-wave pseudo potential approach. The wave functions are expanded in a plane wave basis set defined by use of periodic boundary condition and Bloch's Theorem. The electron-ion potential is described by means of *ab initio* pseudo potentials within both norm-conserving and ultrasoft formulations. Direct energy minimization schemes are used to obtain self-consistently, the electronic wave functions and its corresponding charge density.

Trajectory Model of Ionic Oxide

Conduction geometry of oxygen pathway is predicted by using bond valence sum (BVS). Bond valence method is successfully used to model cation motion in solid material such as K^+ in $KFeAs_2O_7$ [18] and Na^+ in sodium super ionic conductor [19, 20]. BVS states that valence of an atom is sum of the individual bond valences surrounding the atom. BVS is used to map the bond valence sum $m(x, y, z)$ that an O ion would have if placed on an arbitrary point (x, y, z). By moving to the arbitrary point (x, y, z) over a grid covering the whole unit cell volume, probable trajectory for the O ions can be found in γ-$Bi_4V_2O_{11}$ structure. This can be done by following the lower points, $m(x, y, z)$, that are started from a specified position and following a certain initial direction of oxygen. The direction is fixed during travel, and the ion is left free to direct itself to the lowest $m(x, y, z)$ inside a solid angle with an iterative process. This simulates the effect of external electrical force acting on the ion. After a certain trajectory, the ion quite easily reaches a second position in the lattice, which is corresponding usually to a known crystallographic site [21, 22].

Defect Energy and Structure Stability Of Bimevox

The energy defect of BIMEVOX was calculated based on Mott-Littleton method which divides the crystal lattice in the two regions, namely regions I (inner sphere) and II (outer sphere). Region I is the spherical region surrounding defect, which is clearly in relaxation. Meanwhile, the region II is the outer spherical defect that has relatively weak force, which is interpreted with the quasi-continuum approximation method. In this way, the lattice relaxation can be modeled effectively and also the crystal is not as a simple rigid lattice where the diffusion of ions are occured. If the force on the region II is small, it can be assumed that the response of ions in this region is pure harmonic. There are two kinds of defects, namely impurity and vacancy defects. Impurity defect with a defect centre of V^{5+} is substituted partially with dopants of Cu^{2+}, Ga^{3+}, and Ta^{5+}, while the defect of oxygen vacancies are intrinsic defect as well as its are created in equatorial position of oxygen, O(3). The concentration of dopants which substitutes V partially was compensated by reduction of concentrations of oxygen, O(3), to neutralize the charge in BIMEVOX structure. Defect energy calculations were performed at concentrations of 5, 10, 15, and 20% for each dopant, except for Ta^{5+} that was also carried out at the concentration of 25 and 30%.

RESULTS AND DISCUSSIONS

Geometry optimization of the parent structure, γ-$Bi_4V_2O_{11}$ was an initial procedure to check the structure stability. The structure of γ-$Bi_4V_2O_{11}$ reported by Mairesse *et al.* [23], tetragonal, space group *I4/mmm*, cell unit dimension, a = 3.99176(4), b = 3.99176(4), and c = 15.4309(3) Å was used as a starting model. The mean V – O octahedron were encaged between eight Bi sites. However, due to the O(2) and O(3) split-sites, it was observed there were several short O – O contacts, these preclude simultaneous occupation of many of these O sites as shown in Figure 1.

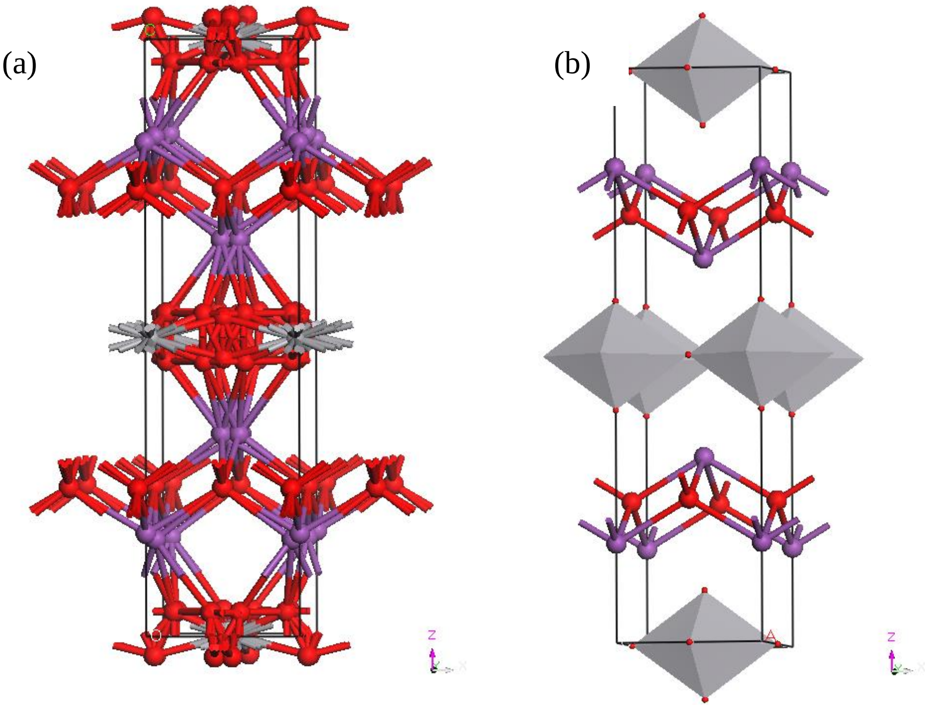


Figure 1. The crystal structures of $Bi_4V_2O_{11}$, (a) average crystallography structure, and b) the refined structure oxygen vacancies were shown as oxygen atoms..

In fact, the V – O environment which appears as an octahedron squashed along the *c* stacking direction must be viewed as the result of superimposed polyhedral. Indeed, by selecting appropriate O sites among those drawn, the classical O environments of the V cation are easily recognised as octahedron, tetrahedron, trigonal bipyramid, and tetragonal pyramid with interatomic distances compatible with O atomic size [24]. Therefore, the structure, that has high symmetry and contain oxygen vacancy, can be represented using by space group *P1* that has no symmetry, as shown at Figure 2.

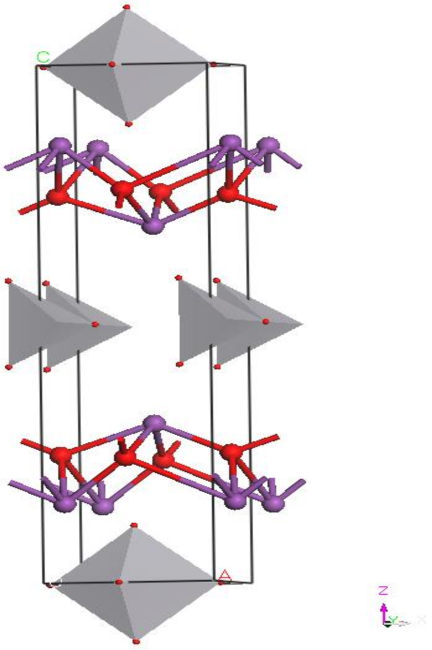


Figure 2. The one possibility of structure that has V - O tetrahedral environment with oxygen vacancy in equatorial site.

The structure in Figure 2 is one of model of structure γ-$Bi_4V_2O_{11}$ showing a special vanadium-oxygen anions coordination environment. The structure that is simulated based on DFT indicates that coordination environment of V cations by O(3) and oxygen vancancy are in good agreement with the crystallography site of γ-$Bi_4V_2O_{11}$ structure, as depicted in Figs. 1*a* and 2. Therefore, the crystal structure (Figure 2) can be used as starting structure to determine activation energy that represent oxygen jump and the easiness of ionic conduction.

Activation Energy

Oxygen ions which surround the vanadium ions (Figure 3) could be devided into two types, namely apical site, O(2), and equatorial site, O(3). Geometry optimization result of γ-$Bi_4V_2O_{11}$ show that the angle that occupied O(3)-V-vacant O(3) against V was 70 degrees, with O(3)-V bond length of 1.72 Å. Throughout this 70 degrees angle, all the different position of O(3) are optimized to describe oxygen pathways in equatorial site as shown in Figure 3.

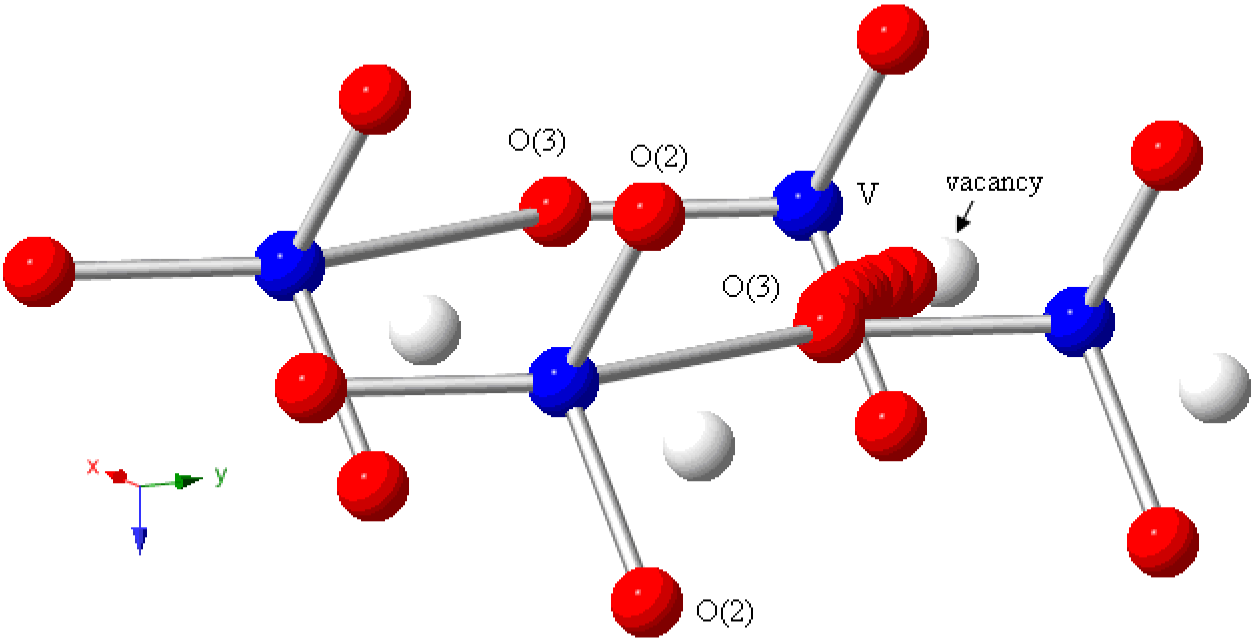


Figure 3. V coordination environments by oxide ions, O(3) equatorial oxygens and O(2) apical oxygens.

Based on result of optimized geometry of γ-$Bi_4V_2O_{11}$, the entalphies of O(3) migration were calculated. The O(3) was moved from one position to the other vacant position. The oxygen position with highest energy, is on the middle between occupied position (initial position) and vacant position, as shown in Figure 4.

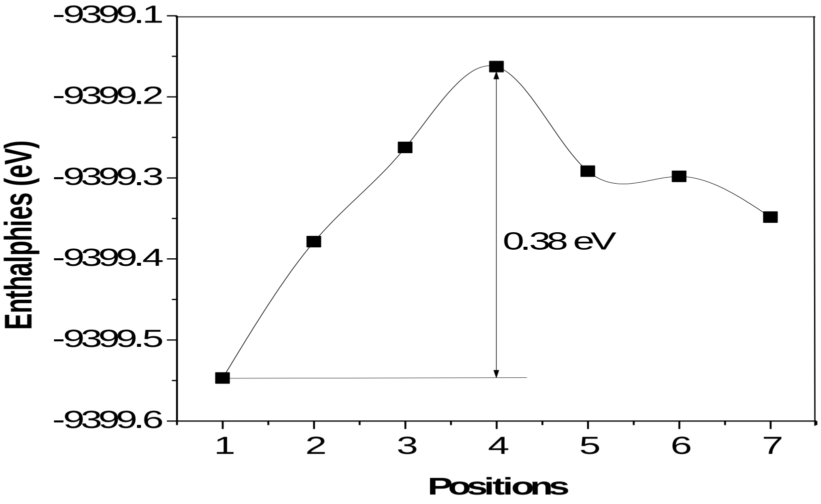


Figure 4. Entalphies of oxygen migration as function of the vacancy position in γ-$Bi_4V_2O_{11}$ structure.

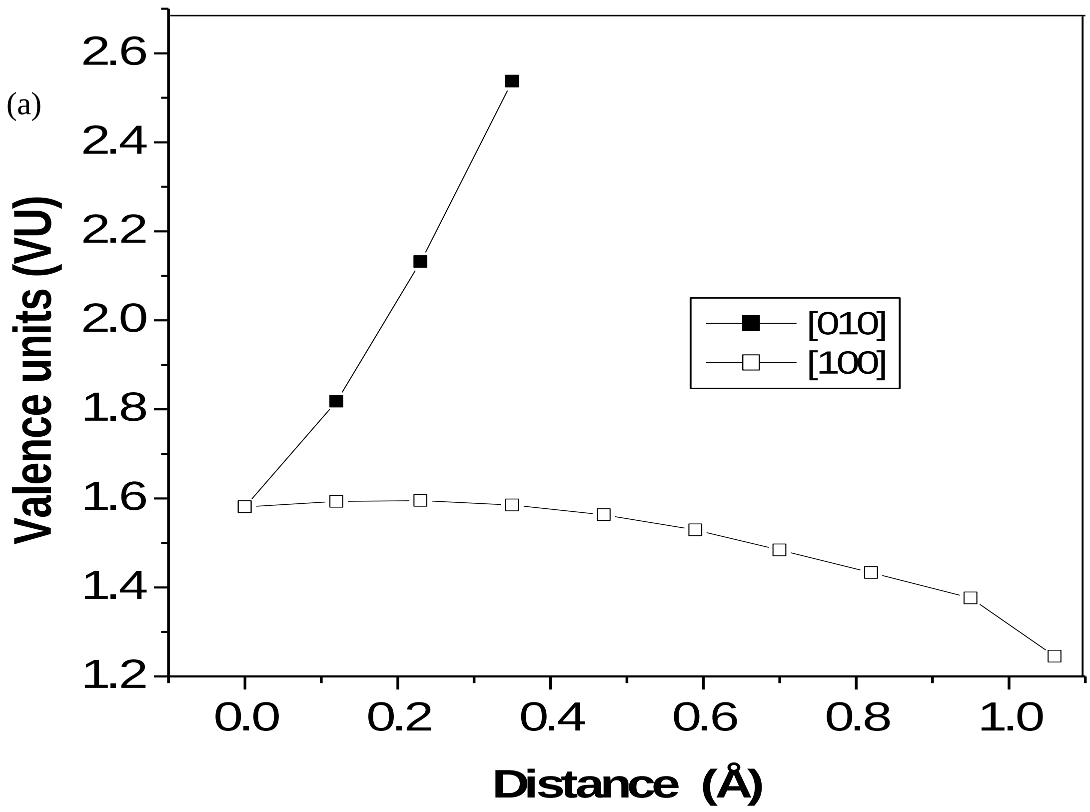
The calculated activation energy of oxygen pathway is 0.38 eV and is in good agreement with experiment results as given in Table 1 [25-28].

Table 1. Activation energies (eV) of oxygen ion motion in γ-$Bi_4V_2O_{11}$ based on this simulation work and these obtained from experiment work.

Calculation (this work)	Experiment [ref.]	Description
0.384	0.3427 [14]	Temperature 500 ˚C, sample obtained from solid state reaction at sintering temperature 800 ˚C for 10 and 12 h
	0.35 [15]	Temperature 600 ˚C, sample obtained from solid state reaction at sintering temperature 840 ˚C for 5 h
	0.3–0.6 [16]	Range of activation energy at high temperature for BIMEVOX
	0.4 [17]	High temperature, sample obtained from solid state reaction at sintering temperature 830 ˚C for 24 h

Trajectory Model of Ionic Oxygen in the Structure of γ-$Bi_4V_2O_{11}$

A high degree of disorder of the γ-$Bi_4V_2O_{11}$ crystal structure (Figure 1) is related to the diffusion of oxide anion in this polymorph. Based on these structures, we selected V-O environment to model the trajectory of O(3). Pathway of oxygen ions in the structure is modelled by using the Jumpiter software based on bond valence sum on various direction. Oxygen movements in the apical environment achieved potential barrier very fast with BVS was 11.758 of 0.131 Å distance. Therefore, oxygen movement was calculated in equatorial site, that can be modeled on the directions of [100], [010], and [*ab*0]. Bond valence sum of trajectory O(3) in these directions were shown in Figure 5.



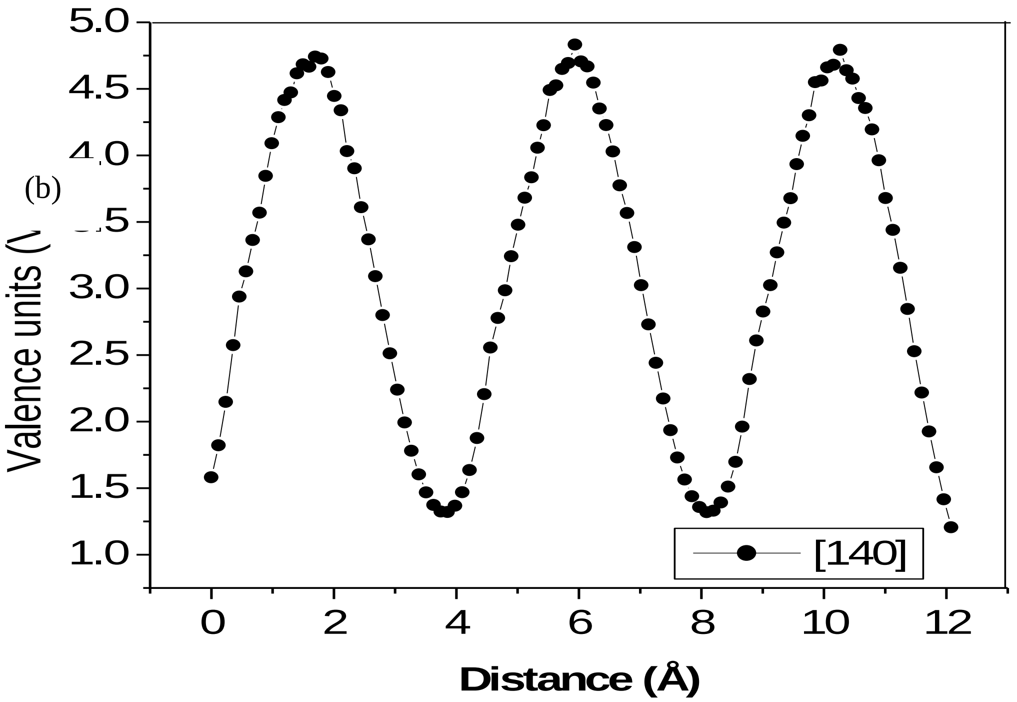


Figure 5. BVS value of O(3) as a function of the distance of the γ-$Bi_4V_2O_{11}$ structure parallel to the directions of *a* [100], *b* [010], and the *ab* [140].

The movement of oxygen ions are difficult in the directions of *a* and *b*. The covered distances for [100] and [010] do not exceed 1,2 and 0,4 Å, respectively. Therefore, an easy conduction path of ionic conductivity in the *γ*-$Bi_4V_2O_{11}$ is in the direction of *ab*, as shown in Figure 6. In $(Bi_2O_2)^{2+}$ layer, lone pair electron of Bi s^2 that lead to like-perovskite layer compress O(2) apical so that bonds of V-O(2) shorter than V-O(3). The compression caused elongation of V-O(3) bond that play important role of the oxide diffusion process in *γ*-$Bi_4V_2O_{11}$. The results show that for O(3) movement to vacant site, from O(3) to other O(3), in the equatorial site, the activation energy, *Ea,* is 0.38 eV.

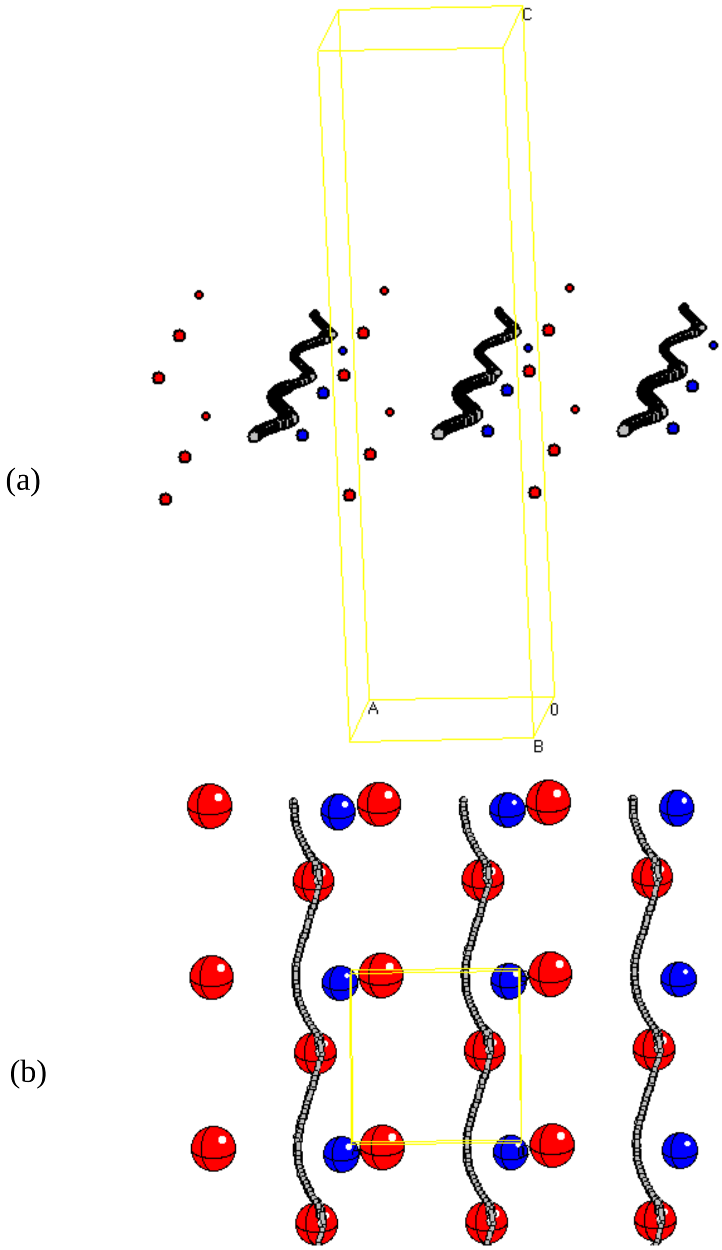


Figure 6. Model of ion conduction pathway of O(3) in γ-$Bi_4V_2O_{11}$ structure parallel to the plane *ab* in two perspectives; (*a)* tube and (*b)* ballstick.

In *γ*-$Bi_4V_2O_{11}$ structure, oxygen ions move more easily in [140] direction, which connect the O(3) with other O(3) through a hopping distance of 3.86 Å. Along these pathways the maximum value of BVS is 4.472, and the mínimum value is 1.320, i.e. within range of +223% to 66% from ideal value of 2. Querfelli e*t al*. reported BVS of potassium cation in $KFeAs_2O_7$ structure were within +197% (max BVS = 1.97) maximum and 89% (min BVS = 0.89) minimum [18]. Mazza reported that the maximum and minimum BVS of sodium cation were 1.4 and mínimum 0.42, i.e. within range of 140% and 42% [19, 20]. Thus, it could be seen that the range BVS values along the pathway are similar to those of other ion conductors.

Oxide ion migration parallel to *ab* plane is in agreement as proposed by I. Abraham and F. Krok [29], where a suitable pathway is available through vacant sites located in equatorial vanadate plane between four vanadium polyhedra. The vacant site of vanadate layer was faced directly with Bi 6s^2 lone pair orbital of $Bi_2O_2^{2+}$ layer, that was coordinated linear. Interaction between layers of $Bi_2O_2^{2+}$ and vanadate in γ-$Bi_4V_2O_{11}$ is ionic. In this site, transient oxide ions can endure electrostatic repulsion, and due to well polarizability of the Bi 6s^2 lone pair orbital, so this route in equatorial site can avoid oxide ions more close to vanadium ions [29].

Defect Energy and Structure Stability of BIMEVOX

The calculation of defect energy is an important step to treat the lattice relaxation of point defect or migrating ion. In this study, defect energy of BIMEVOX is calculated based on Mott-Littleton method. The number of ions involved in this defect energy calculations are 5,604 ions for region I and 103,016 ions for region II, with each radius is and 37 Å, respectively. Defect energy calculation results were summarized in Figure 7.

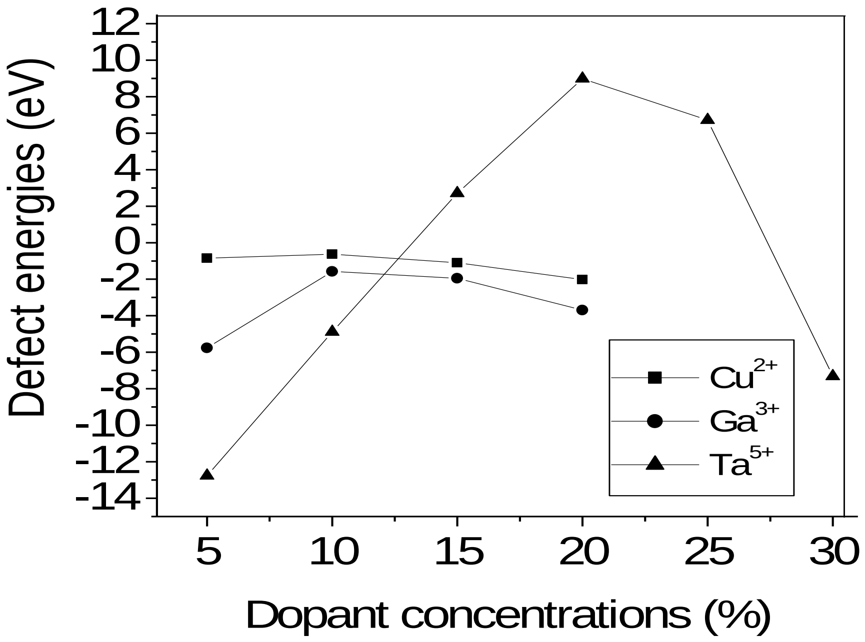


Figure 7. Energy defect in the region II as function of dopant concentration. BIMEVOX structure is expected to more conductive at dopant concentration of 10% Cu, 15% Ga, and 20% Ta.

The results of the defect energy calculations show that the defect energy values of region II varies according to the dopant type and concentration. Energy defect increases up to consentration of 10% for all dopants. However, for Ta^{5+}, defect energy increases with the concentration up to 20%. This is as expected because of Ta is isovalence to V, with valence =

+5. Defect energy maximum values were reached at concentrations of 10% for Cu and Ga, and 20% for Ta, with values of -0.63, -1.57 and 8.98 eV, respectively. BICUVOX and BIGAVOX defect energies are more negative at a concentration more than 10%, and the BITAVOX defect energies have a highest negative values at concentrations of 5 and 30% Ta. The negative values of defect energy show that response of ion is pure harmonic and is unstable. Howerer, the BIMEVOXes can be synthesized at the concentration [8, 30-32].

Oxygen vacancies can be varied in accordance with the dopant valence and concentration. The dopant concentration increase the amount of oxygen vacancies in positions O(3). The preference of dopants affect symmetry and connectivity of polyhedral in perovskite-like layer. Consequently, the performance of ionic conductivity is also expected to significantly depend on the defect structure and the effect of trapping on the diffusion pathway of oxygen [14]. Therefore, a stable structure is achieved when each dopant is at a certain concentration. Based on the defect energy values in this work, concentration of dopants that stabilize γ-$Bi_4V_2O_{11}$ and were predicted have highest conductivity are 10% for Cu, 10% for Ga, and 20% for Ta. At these concentrations, cation polarisability of dopants are predicted to have achieve maximum value so that facilitate the oxide ion diffusion process in the like-perovskite layers. Again, we predict that sequences of decreasing conductivity of BICUVOX, BIGAVOX, and BITAVOX are 10>15>20% for Cu; 10>15>20% for Ga; and 20>25>15>30% for Ta, respectively, as Figure 7. These are in agreement with the experimental results reported by R. Kant, *et al*., S. Lajure *et al*., and V. Murasheva *et al*., [20-23]. At concentrations more than 10% Cu, ionic conductivity of BICUVOX decrease with the encreasing vacancy because of its like-provskite volume is increased as reported by Axel [24].

Concentration value of 10% Cu in this study is in good agreement with experimental results reported by R. Kant, *et al*. [20] which showed that the stable structure of BICUVOX is achieved at 10%, which has a grain pattern and uniform in size with adequate porosity compared with the concentration of 15 and 20%. Concentration of 20% Ta also in good agreement with the experimental results reported by S. Lajure, *et al*. which states that the best conductivity for BITAVOX achieved at a concentration of 20% Ta [21]. BIGAVOX has also the highest conductivity at a concentration of 10% Ga for the gamma phase. According to R. Kant, *et al.* BIGAVOX has highest conductivity at 10% for beta phase not gamma phase [22]. While, according to V. Murasheva *at el*. BIGAVOX phase was gamma at 10% Ga with more uniform grain [23].

CONCLUSIONS

Computational simulation of ionic conductivity of BIMEVOX and γ-$Bi_4V_2O_{11}$, have been performed using DFT, Mott-Littleton and BVS methods. The obtained activation energy for γ-$Bi_4V_2O_{11}$ is 0.38 eV and in good agreement with those of experimental results. Pathways of oxygen occur within equatorial site on coordination environment of V - O. Oxygen are easily move on [140] direction that is parallel to *ab* plane, with minimum BVS value of 1.320. Defect simulation results with the Mott-Littleton method showed that the total energy in region II, which describes the harmonic motion, is achieved at concentrations of 10, 10, and 20%, respectively for Cu^{2+}, Ga^{3+}, and Ta^{5+}. Concentration values of Cu^{2+}, Ga^{3+} and Ta^{5+} are in good agreement with the experiment results where the highest ionic conductivity obtained.

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I have read the manuscript with the title "HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION", the work seems to be interesting and looks important. In my opinion, the manuscript should be masivelly rewritten due to the following reasons:

General

1. Some typographical errors are spotted, like "dopents".
2. Use consistent unit. There are mixing between temperature unit of K and °C.
3. The references should follow IJC format.
4. Check the English grammar.

Scientific points

1. The reason to investigate the γ phase of Bimevox seems to contradict with the reason that bimevox is more efficient than conventional SOFC materials at low temperature. The γ phase is stable at higher temperature. Why would authors not investigate the lower temperature phases?
2. The experimental works related to the present work are too old. There should be more recent works dealing with bimevox if indeed the materials are useful and technologically applicable.
3. For me, the computational methodologies are a still unclear. The first part of the methods explains the calculations of the activation energy. What kind of activation energy is not explicitly mentioned. Is it oxygen migration activation energy? If so, in my opinion, the term should be changed into oxygen atom/ion migration barrier. I also believe that the authors employed the nudge elastic band method to find the minimum energy pathway. If so, mention it in the text.
4. Still in the same section, I found that many important details are missing. What DFT functional was used in the current work? If the authors employed planewave basis set, mention the kinetic energy cutoff. Also, the k-point sampling method and k-point grid must be mentioned. On the other hand, there are many unecessary details that are mentioned in the text such as "… density functional theory (DFT) that states the total energy of the system of electrons in the external potential is a unique function of the ground state density…" and the like. Such an information is generally known. The section should be rewritten systematically to show the most important details.
5. The BVS method should have some brief theoretical background. Add some relevant equations to clarify the written text. Also, add some more recent "successful" works based on the BVS method if indeed the method is a best method for this kind of work.
6. Add references of the Mott-Littleton method. Also, add some relevant equations of this method.
7. The equation to calculate the defect energy should be mentioned. Example: Malyi, et al Solid State Ionics 212 (2012) 117–122.
8. In my understanding, the experiments were conducted at ~500 °C. However, the computational methodologies do not mention any temperature. In what temperature were the calculations conducted? What is the effect of the experimental temperature to the quantitative results of the computational study?
9. Does the Figure 1 show the γ phase?
10. The y-axis on the Figure 4 should be relative energy, i.e. the lowest energy configuration should be shifted to 0.
11. There should be any figures showing each position of oxygen in addition to the graph of Figure 4.

12. I think the comparison between the theoretical results with the experimental results as listed in table 1 is not a fair comparison. The computational results only calculated the oxygen migration barrier and pathway in $Bi_4V_2O_{11}$ (Bivo ?) while the experimental results show the Bimevox materials, i.e. has some metal dopants. I believe that there are significant effects of addition of metal into the structure to the migration barrier (cf. Introduction). If possible also calculate the oxygen migration barrier and pathway of the bimevox.
13. The authors should emphasize the theoretical results to the perspectives towards experiments, i.e. so what if the results are in good agreement with the experiment results? What can the readers learn about the conclusions?

HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION

ABSTRACT

BIMEVOX had potential to play an important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, oxide ion migrations of γ-$Bi_2VO_{5.5}$ and BIMEVOX were simulated using density function theory (DFT), Mott-Littleton method and molecular dynamic simulation. In γ-$Bi_2VO_{5.5}$, there were oxygen vacancies at the equatorial position in the vanadate layers. These vacancies could facilitate oxide ions migration. The Enthalpy of the oxide migration for γ-$Bi_2VO_{5.5}$based on DFT calculation was 0.38 eV, which was in a good agreement with experimental results. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with Cu^{2+}, Ga^{3+}, and Ta^{5+}. Defect simulation results using the Mott-Littleton method showed that the total maximum energies of region II are achieved at concentrations of 10, 10, and 20%, respectively for Cu^{2+}, Ga^{3+}, and Ta^{5+}. The calculated concentration of Cu^{2+}, Ga^{3+}, and Ta^{5+}were in a good agreement with those of experiment results, where the highest ionic conductivity obtained. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME= Cu and Ta) respectively were 0.19, 0.21, and 0.10 eV, close to experimental values.

Keywords: simulation, defect, γ-$Bi_2VO_{5.5}$ and BIMEVOX, ionic migration.

INTRODUCTION

Solid electrolyte materials with high oxide ion conductivity ~~at low temperature are~~ intensively investigated in order to have solid oxide fuel cell (SOFC)~~ capable of operating at low temperature~~. One of oxide materials that had high oxide ion conductivity and potential application was $Bi_2V_{1-x}Me_xO_{5.5-σ}$ (BIMEVOX) ~~with~~ where ME was dopant [1-3]~~= Ta, Cu, Ga, Ta, etc~~. Dopant at a certain concentration play an important role in improving the ease of oxygen ions migrate of $Bi_2VO_{5.5}$ [4-5]. Therefore, in addition to the migration path of oxygen ions, the search for a type of dopant with a certain concentration was needed to obtain BIMEVOX with high conductivity. Computational simulation method could be conducted first to predict the ease of migration of ion. ~~As comparison with the materials widely used solid electrolyte material, such~~

~~as yttria stabilized zirconia (YSZ), BIMEVOX has ionic conductivity of 1x10^{-2} Scm^{-1}, which is aroundthree orders of magnitude larger than YSZ at same temperature of 300 °C [1]. Therefore BIMEVOX has potential application as electrolyte in SOFC working at low temperature. BIMEVOX also has potential application as oxygen separation devices and for catalytic inorganic membrane reactors (CIMRs) [2].~~

BIMEVOX was family of oxides derived from $Bi_2VO_{5.5}$and obtained by doping into the vanadium site of $Bi_2VO_{5.5}$ by aliovalent or isovalent metal cations (ME). The structure of $Bi_2VO_{5.5}$ could be derived from Bi_2MoO_6 and δ-Bi_2MoO_6 by formation of oxygen vacancies in the metal oxygen layers; thus the compound can be formulated as $(Bi_2O_2)(VO_{3.5}\square_{0.5})$, where $\square$ was corresponding to the intrinsic oxygen vacancies [6, 7].

The $Bi_2VO_{5.5}$ goes to several structural transformations and known had several polymorphs, but essentially there were only three main polymorphs, namely α, β, and γ-$Bi_2VO_{5.5}$with the transformations: $\alpha \rightarrow \beta$ at 720 K and $\beta \rightarrow \gamma$ at 840 K. The structures of α and β-phases were more ordered, larger in unit cell and had lower conductivity. At the high temperature, γ-phase wasformed and had conductivity of 0.2 Scm^{-1} at 943 K [8]. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with other metal cations (ME) [9-10]. The substitution do not only stabilize the structure but also increase ionic conductivity due to the creation of vacancies [11]. Therefore, the computational simulation carried out in this study is the gamma phase of $Bi_2VO_{5.5}$ and BIMEVOX (ME = Cu^{2+}, Ga^{3+} and Ta^{5+}). ~~Transition metals such as Cu, and Zn can be used to substitute V in γ-$Bi_2VO_{5.5}$ which lead to stabilization of the tetragonal structure and also gives high oxide ion conductivity at intermediate temperature, 227-677 °C [11].~~

The experimental results of BIMEVOX compounds showed the contribution of electrons that affected BIMEVOX conductivity [12]. Moreover, the texture of compounds, surface conditions, pore existence, and the presence of impurities affect ionic conductivity. Single phase of BITAVOX could not be obtained by synthesis [13]. Dereerper *et al.* reported that BITAVOX conductivy increase with the increase in Ta dopant concentration. BIGAVOX had a smaller conductivity due to the contribution of electron conductivity [12]. Therefore, the single phase of the gamma-$Bi_2VO_{5.5}$ and BIMEVOX (Cu^{2+}, Ga^{3+} and Ta^{5+}) through computational modeling and simulation was important to be conducted to predict the possibility of ease of migration of oxygen ions without the presence of electron conductivity.

~~Polarizability of dopants in the γ-$Bi_2VO_{5.5}$ plays an important role in the stabilization of the structure as well as to oxide conductivity. For example, the ionic conductivity of $Bi_2Cu_{0.1}V_{0.9}O_{5.5-\delta}$ is higher than $Bi_2Zn_{0.1}V_{0.9}O_{5.5-\delta}$ since the polarizability of Cu^{2+} is larger than Zn^{2+} [12]. Therefore the cation ability to polarize oxygen can also facilitate hopping of oxygen in~~

~~the structure [8]. Meanwhile, the ionic radius of metal dopans are also important to the conductivity. This mean that the dopant with ionic radius close to the V^{5+} radius could enhance the conductivity [13].~~

Experimental studies on the oxide ionic conductivity of BIMEVOX has been reported, elsewhere [14]. However, the experimental study could not reveal the detail of the mechanism of oxide ioni conductivity and role of dopant in the BIMEVOX on the structural properties. Computational studies could be used to study many material properties efficiently in order to save time and cost as well as to provide more detail mechanism in the atomic level. Some computation study on the layered structure of Aurivillius phases similar to BIMEVOX has been carried out and reported [15, 16]. It could reveal defect energies and maximum dopant concentrations in Aurivillius as ferroelectric material. From our best knowledge, the computational study on BIMEVOX is not reported yet.

Here, we report the computational study on BIMEVOX and its parent structure that cover trajectory of ionic oxide in γ-$Bi_2VO_{5.5}$ and defect energy ~~and stability structure~~ of BIMEVOX. The study was aimed to investigate the oxide ion pathways that are possible in the V^{5+} coordination environments of γ-$Bi_2VO_{5.5}$ as well as to predict dopant concentrations of Cu^{2+}, Ga^{3+} and Ta^{5+} that give the higher ionic conductivity. Subsequently, transport properties and activation energy of migration of oxygen ions of parent compound and BIMEVOX (ME = $Cu^{2+}$and Ta^{5+}) which were predicted to have the highest ionic conductivity were simulated using the molecular dynamics method. Those dopants were selected because of its ionic radius close to ionic radius of V^{5+}.This mean that the dopant with ionic radius close to the V^{5+} radius could enhance the conductivity [17].

METHODS

Enthapy of Oxide Ion Migration

The enthalpies of oxide ion migration of γ-$Bi_2VO_{5.5}$ were calculated by using computational simulation method that is based on density functional theory (DFT). This simulation used CASTEP code of Material Studio Modeling from Accerys, series number 3.2.00, in Politecnico di Torino [18]. Methodology for electronic structure calculations in CASTEP is as follows: set of one-electron Schrodinger (Kohn-Sham) equations are solved using the plane-wave pseudo potential approach. The wave functions are expanded in a plane wave basis set defined by use of periodic boundary condition and Bloch's Theorem. The electron-ion potential is described by means of *ab initio* pseudo potentials within both norm-conserving and ultrasoft formulations. Direct energy minimization schemes are used to obtain self-consistently, the electronic wave functions and its corresponding charge density. Lattice optimisation is initially performed using exchange–correlation energy functions of Perdew–Burke–Ernzerhof (GGA-PBE). Structural optimisation is_implemented to determine the best functional approximation to perform in examining the enthalpy of γ-$Bi_2VO_{5.5}$at various oxygen positions of the tetragonal vanadate layer. A k-point grid of 1×1×1 generated using theMonkhorst–Pack method for Brillouin zone sampling withan energy cut-off of 600 eV.

~~Trajectory Model of Ionic Oxide~~

~~Conduction geometry of oxygen pathway is predicted by using bond valence sum (BVS). Bond valence method is successfully used to model cation motion in solid material such as K^+ in $KFeAs_2O_7$ [18] and Na^+ in sodium super ionic conductor [19, 20]. BVS states that valence of an atom is sum of the individual bond valences surrounding the atom. BVS is used to map the bond valence sum $m(x, y, z)$ that an O ion would have if placed on an arbitrary point (x, y, z). By moving to the arbitrary point (x, y, z) over a grid covering the whole unit cell volume, probable trajectory for the O ions can be found in γ-$Bi_4V_2O_{11}$ structure. This can be done by following the lower points, $m(x, y, z)$, that are started from a specified position and following a certain initial direction of oxygen. The direction is fixed during travel, and the ion is left free to direct itself to the lowest $m(x, y, z)$ inside a solid angle with an iterative process. This simulates the effect of external electrical force acting on the ion. After a certain trajectory, the ion quite easily reaches a second position in the lattice, which is corresponding usually to a known crystallographic site [21, 22].~~

Atomistic simulation and Molecular Dynamic

The main samples used in this simulation are of two types, namely (i) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with an I4/mmm space group as reported by Mairesse et al. [17] and (ii) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with *P*1 space group modified from the first structure. The two structures were then doped with dopant (ME) of Cu, Ga, and Ta to obtain BIMEVOX compounds. In the first structure, the simulation method applied is atomistic simulation using GULP [19]. The simulation aims to calculate defect energy while predicting the ease of migration of oxygen ion in BIMEVOX based on the increase in dopant concentration. While the second structure applied molecular dynamics to determine the nature of transport or activation energy of the migration of oxygen ions using the DLPOLY code [20].

Both simulation methods use Buckingham's short range potential defined:

$$\theta_{ij} = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \qquad (1)$$

where A_{ij},ρ_{ij},andC_{ij}were constant parameters and r_{ij} was the distance between *i* and *j*ions. The first term in equation (1) describes short-range repulsion, while the second term shows induced dipole (van der Waals interaction).

Using DL_POLY, different defect concentrations were simulated by creating supercell of 4×4×4 containing dopant concentrations (10% Cu and 20% Ta) and the respective amount of oxygen vacancies. The simulations were carried out for a step time of 0.0002 ps with ensemble of constant temperature and volume (NVT) and algoritma of leap frog that applied on simulation box of 1088 ions.

Defect Energy of BIMEVOX

Calculation of energy defects in atomistic simulations is performed on the average structure of γ-$Bi_2VO_{5.5}$and BIMEVOX with space group I4/mmm. The energy defect of BIMEVOX was calculated based on Mott-Littleton method which divides the crystal lattice in the two regions, namely regions I (inner sphere) and II (outer sphere). Region I is the spherical region surrounding defect, which is clearly in relaxation. Meanwhile, the region II is the outer spherical defect that has relatively weak force, which is interpreted with the quasi-continuum approximation method. In this way, the lattice relaxation can be modelled effectively and also the crystal is not as a simple rigid lattice where the diffusion of ions are occurred. If the force on the region II is small, it can be assumed that the response of ions in this region is pure harmonic. There are two kinds of defects, namely impurity and vacancy defects. Impurity defect with a defect centre of V^{5+} is substituted partially with dopants of Cu^{2+}, Ga^{3+}, and Ta^{5+}, while the defect of oxygen vacancies are intrinsic defect as well as its are created in equatorial position of oxygen, O(3). The concentration of dopants which substitutes V partially was compensated by reduction of concentrations of oxygen, O(3), to neutralize the charge in BIMEVOX structure. Defect energy calculations were performed at concentrations of 5, 10, 15, and 20% for each dopant, except for Ta^{5+} that was also carried out at the concentration of 25 and 30%.

RESULTS AND DISCUSSIONS

Geometry optimization of the parent structure, γ-$Bi_2VO_{5.5}$ was an initial procedure to check the structure stability. The structure of γ-$Bi_2VO_{5.5}$ reported by Mairesse *et al.* [17], tetragonal, space group *I*4/mmm, cell unit dimension, *a* = 3.99176(4), *b* = 3.99176(4), and *c* = 15.4309(3) Å was used as a starting model. The mean V – O octahedron were encaged between eight Bi sites. However, due to the O(2) and O(3) split-sites, it was observed there were several short O – O contacts, these preclude simultaneous occupation of many of these O sites as shown in Figure 1.

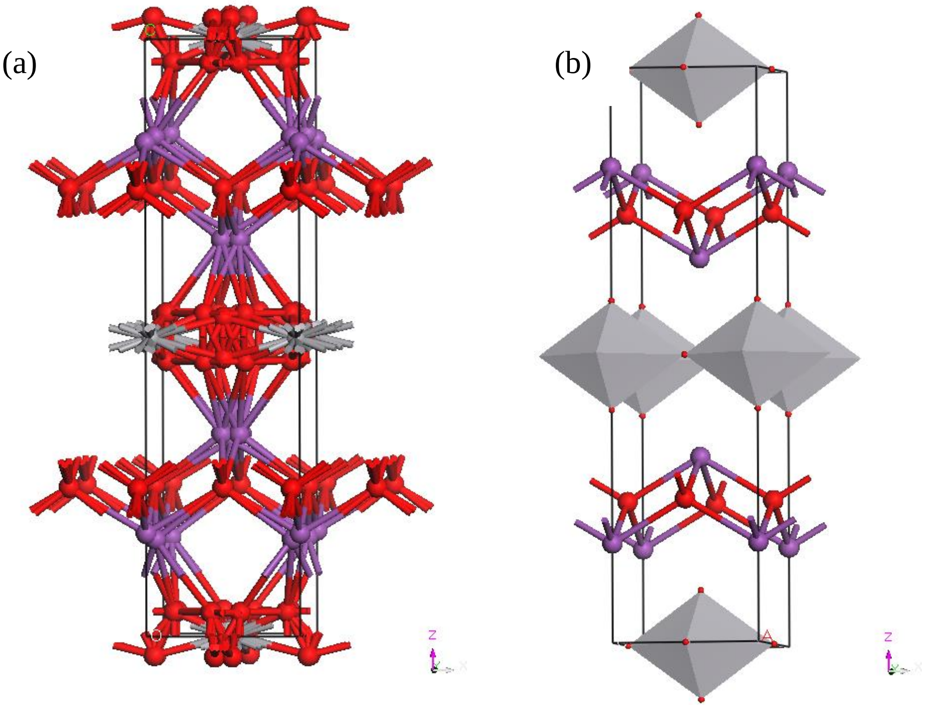


Figure 1. The crystal structuresof $Bi_2VO_{5.5}$,(a) average crystallography structure, and b) the refined structure oxygen vacancies were shown as oxygen atoms..

In fact, the V – O environment which appears as an octahedron squashed along the *c* stacking direction must be viewed as the result of superimposed polyhedral. Indeed, by selecting appropriate O sites among those drawn, the classical O environments of the V cation are easily recognised as octahedron, tetrahedron, trigonal bipyramid, and tetragonal pyramid with interatomic distances compatible with O atomic size [21]. Therefore, the structure, that has high symmetry and contain oxygen vacancy, can be represented using by space group *P1* that had no symmetry, as shown at Figure 2.

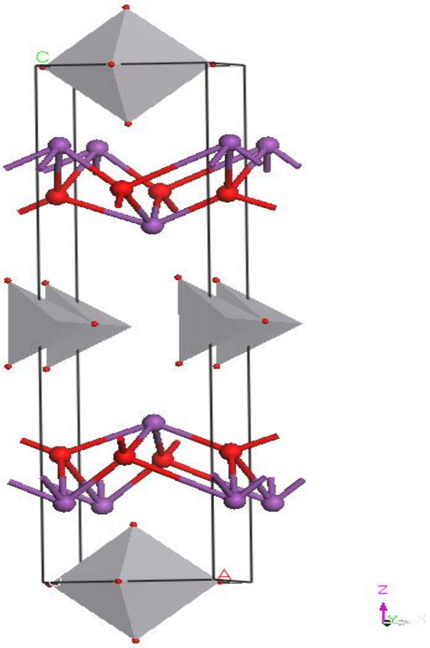


Figure 2. The one possibility of structure that has V - O tetrahedral environment with oxygen vacancy in equatorial site.

The structure in Figure 2 was one of model of structure γ-$Bi_2VO_{5.5}$ showing a special vanadium-oxygen anions coordination environment. The structure that is simulated based on DFT indicates that coordination environment of V cations by O(3) and oxygen vancancy are in good agreement with the crystallography site of γ-$Bi_2VO_{5.5}$ structure, as depicted in Figures 1*a* and 2.Therefore, the crystal structure (Figure 2) can be used as starting structure to determine activation energy that represent oxygen jump and the easiness of ionic conduction.

Pathway of Ion oxide Migration of $Bi_2VO_{5.5}$

Oxygen ions which surround the vanadium ions (Figure 3) could be devided into two types, namely apical site, O(2), and equatorial site, O(3). Geometry optimization result of γ-Bi2VO5.5 show that the angle that occupied O(3)-V-vacant O(3) against V was 70 degrees, with O(3)-V bond length of 1.72 Å. Throughout this 70 degrees angle, all the different position of O(3) are optimized to describe oxygen pathways in equatorial site as shown in Figure 3.

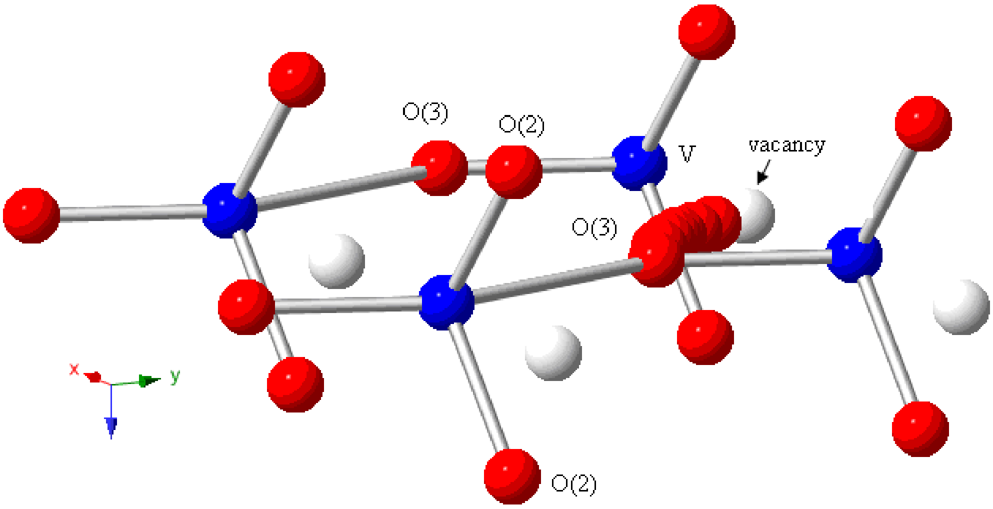


Figure 3. V coordination environments by oxide ions, O(3) equatorial oxygens and O(2) apical oxygens.

Based on result of optimized geometry of γ-$Bi_2VO_{5.5}$, the entalphies of O(3) migration were calculated. The O(3) was moved from one position to the other vacant position. The oxygen position with highest energy, is on the middle between occupied position (initial position) and vacant position, as shown in Figure 4.

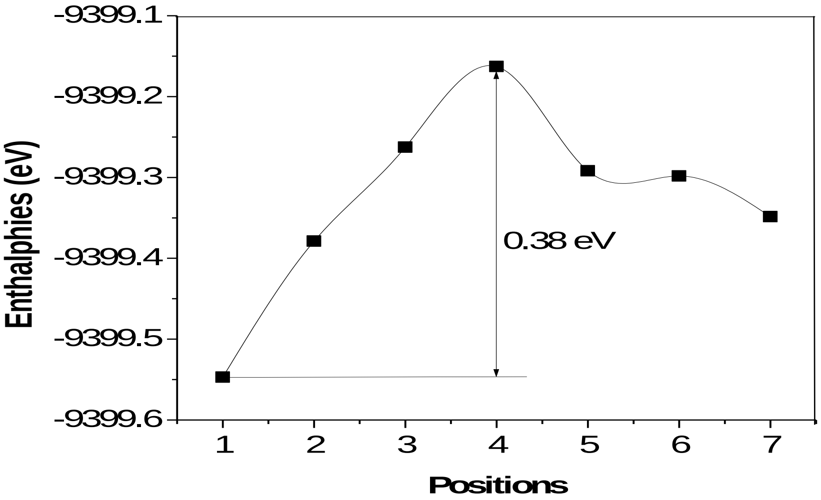


Figure 4. Entalphies of oxygen migration as function of the vacancy position in γ-$Bi_2VO_{5.5}$ structure.

The calculated activation energy of oxygen pathway was 0.38 eV and is in good agreement with experiment results as given in Table 1.

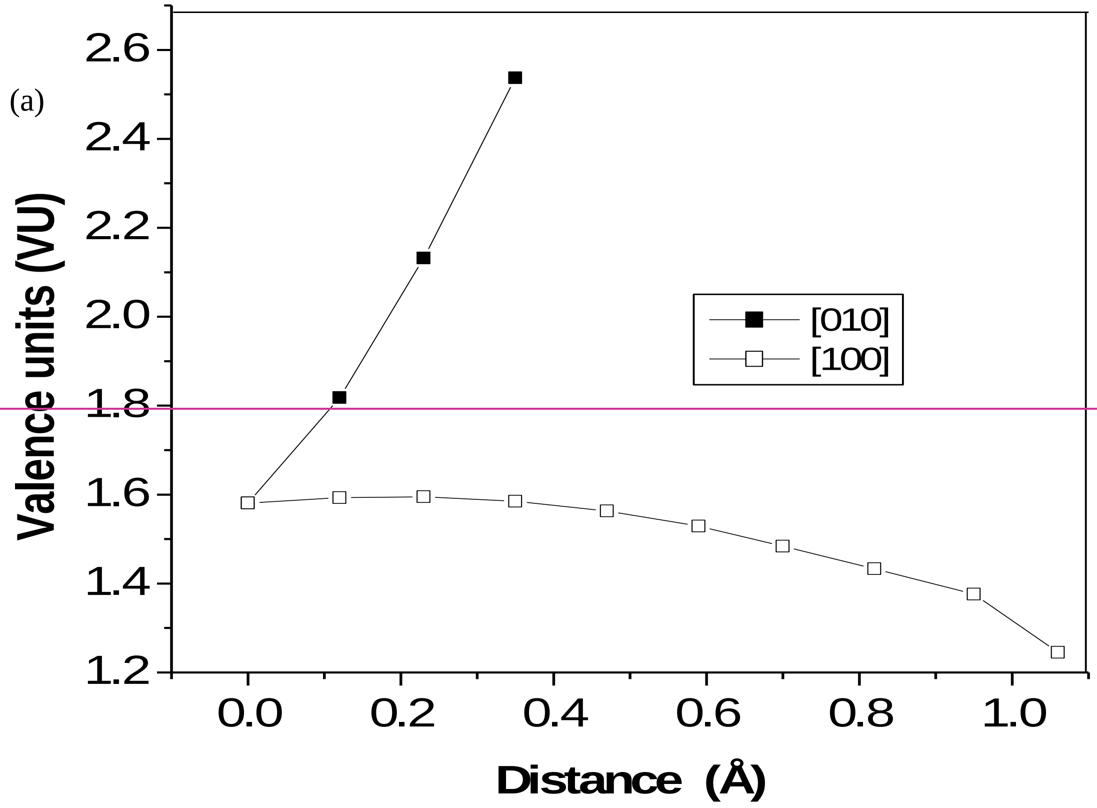
Table 1. Activation energies (eV) of oxygen ion motion in γ-$Bi_2VO_{5.5}$ based on this simulation work and these obtained from experiment work.

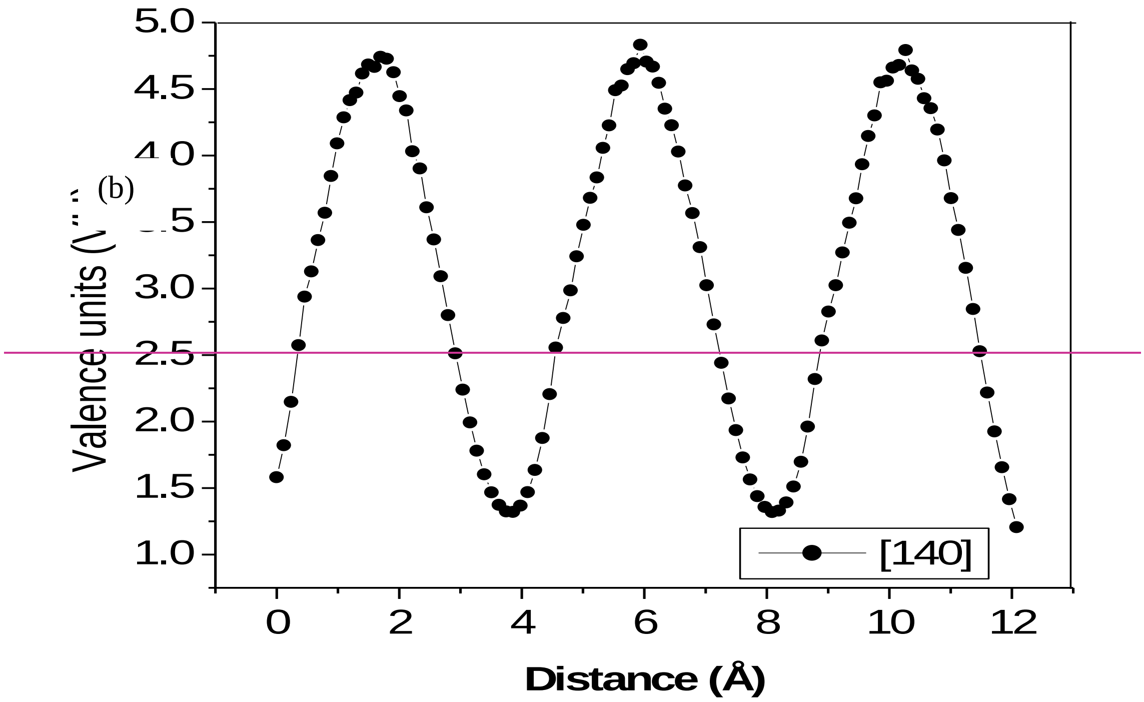
Calculation (this work)	Experiment [ref.]	Description
0.384	0.3427 [14]	Temperature 500 ˚C, sample obtained from solid state reaction at sintering temperature 800 ˚C for 10 and 12 h
	0.35 [15]	Temperature 600 ˚C, sample obtained from solid state reaction at sintering temperature 840 ˚C for 5 h
	0.4 [22]	High temperature, sample obtained from solid state reaction at sintering temperature 830 ˚C for 24 h

~~Trajectory Model of Ionic Oxygen in the Structure of γ-Bi2VO5.5~~

~~A high degree of disorder of the γ-Bi2VO5.5crystal structure (Figure 1)is related to the diffusion of oxide anion in this polymorph. Based on these structures, we selected V-O environment to model the trajectory of O(3). Pathway of oxygen ions in the structure is modelled~~

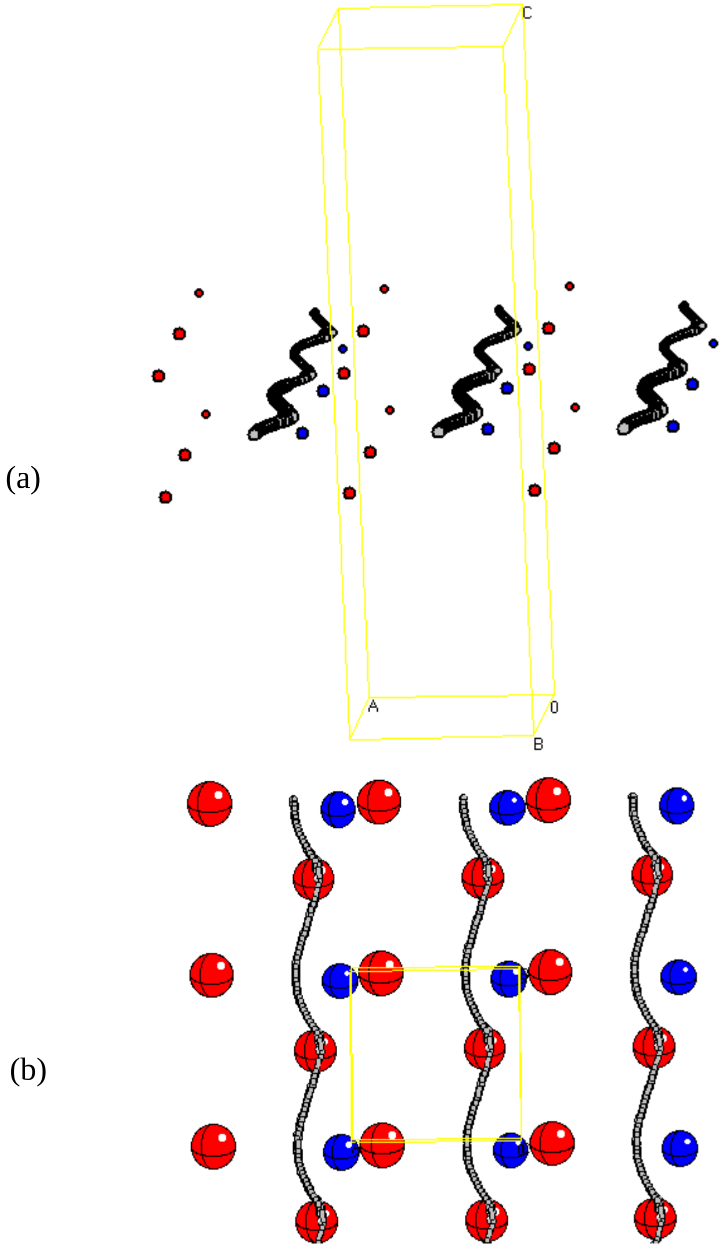
~~by using the Jumpiter software based on bond valence sum on various direction. Oxygen movements in the apical environment achieved potential barrier very fast with BVS was 11.758 of 0.131 Å distance. Therefore, oxygen movement was calculated in equatorial site, that can be modeled on the directions of [100], [010], and [*ab*0]. Bond valence sum of trajectory O(3) in these directions were shown in Figure 5.~~





~~**Figure 5**. BVS value of O(3) as a function of the distance of the γ-Bi2VO5.5 structure parallel to the directions of a [100], *b* [010], and the *ab* [140].~~

~~The movement of oxygen ions are difficult in the directions of *a* and *b*. The covered distances for [100] and [010] do not exceed 1,2 and 0,4 Å, respectively. Therefore, an easy conduction path of ionic conductivity in the *γ*-Bi2VO5.5 is in the direction of *ab*, as shown in Figure 6. In $(Bi_2O_2)^{2+}$layer, lone pair electron of Bi s^2 that lead to like-perovskite layer compress O(2) apical so that bonds of V-O(2) shorter than V-O(3). The compression caused elongation of V-O(3) bond that play important role of the oxide diffusion process in *γ*-Bi2VO5.5. The results show that for O(3) movement to vacant site, from O(3) to other O(3), in the equatorial site, the activation energy, *Ea,* is0.38 eV.~~



~~**Figure 6**. Model of ion conduction pathway of O(3) in γ-Bi2VO5.5 structure parallel to the plane *ab* in two perspectives; (*a*) tube and (*b*) ballstick.~~

~~In γ-Bi2VO5.5 structure, oxygen ions move more easily in [140] direction, which connect the O(3) with other O(3) through a hopping distance of 3.86 Å. Along these pathways the maximum value of BVS is 4.472, and the mínimum value is 1.320, i.e. within range of +223% to 66% from ideal value of 2. Querfelli e*tal*. reported BVS of potassium cation in KFeAs$_2$O$_7$ structure were within +197% (max BVS = 1.97) maximum and 89% (min BVS = 0.89) minimum [18]. Mazza reported that the maximum and minimum BVS of sodium cation were 1.4 and mínimum 0.42, i.e. within range of 140% and 42% [19, 20]. Thus, it could be seen that the range BVS values along the pathway are similar to those of other ion conductors.~~

~~Oxide ion migration parallel to *ab* plane is in agreement as proposed by I. Abraham and F. Krok [29], where a suitable pathway is available through vacant sites located in equatorial vanadate plane between four vanadium polyhedra. The vacant site of vanadate layer was faced directly with Bi 6s^2 lone pair orbital of $Bi_2O_2^{2+}$ layer, that was coordinated linear. Interaction between layers of $Bi_2O_2^{2+}$ and vanadate in *γ*-Bi2VO5.5 is ionic. In this site, transient oxide ions can endure electrostatic repulsion, and due to well polarizability of the Bi 6s^2 lone pair orbital, so this route in equatorial site can avoid oxide ions more close to vanadium ions [29].~~

Defect Energy ~~and Structure Stability~~ of BIMEVOX

The calculation of defect energy is an important step to treat the lattice relaxation of point defect or migrating ion. In this study, defect energy of BIMEVOX is calculated based on Mott-Littleton method. The number of ions involved in this defect energy calculations are 5,604 ions for region I and 103,016 ions for region II, with each radius is and 37 Å, respectively. Defect energy calculation results were summarized in Figure 5.

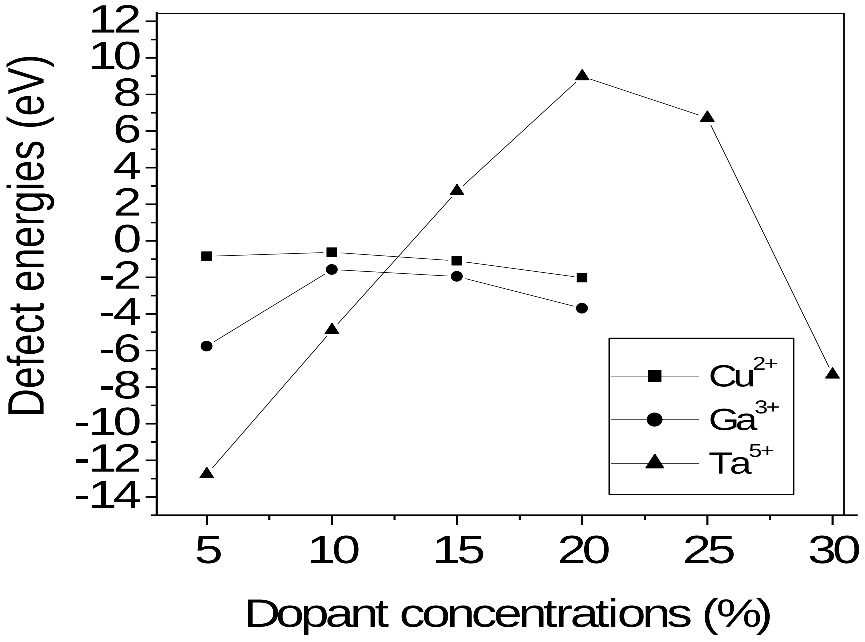


Figure 5. Energy defect in the region II as function of dopant concentration. BIMEVOX structure is expected to more conductive at dopant concentration of 10% Cu, 15% Ga, and 20% Ta.

The results of the defect energy calculations show that the defect energy values of region II varies according to the dopant type and concentration. Energy defect increases up to consentration of 10% for all dopants. However, for Ta^{5+}, defect energy increases with the concentration up to 20%. This is as expected because of Ta is isovalence to V, with valence = +5. Defect energy maximum values were reached at concentrations of 10% for Cu and Ga, and 20% for Ta, with values of -0.63, -1.57 and 8.98 eV, respectively. BICUVOX and BIGAVOX defect energies are more negative at a concentration more than 10%, and the BITAVOX defect energies have a highest negative values at concentrations of 5 and 30% Ta. The negative values of defect energy show that response of ion is pure harmonic and is unstable. Howerer, the BIMEVOXes can be synthesized at the concentrations.

Oxygen vacancies can be varied in accordance with the dopant valence and concentration. The dopant concentration increase the amount of oxygen vacancies in positions O(3). The preference of dopants affect symmetry and connectivity of polyhedral in perovskite-like layer. Consequently, the performance of ionic conductivity is also expected to significantly depend on the defect structure and the effect of trapping on the diffusion pathway of oxygen [14].Therefore, a stable structure is achieved when each dopant is at a certain concentration. Based on the defect energy values in this work, concentration of dopants that stabilize *γ*-Bi2VO5.5 and were predicted have highest conductivity are 10% for Cu, 10% for Ga, and 20% for Ta. At these concentrations, cation polarisability of dopants are predicted to have achieve maximum value so that facilitate the oxide ion diffusion process in the like-perovskite layers. Again, we predict that sequences of decreasing conductivity of BICUVOX, BIGAVOX, and BITAVOX are 10>15>20% for Cu; 10>15>20% for Ga; and 20>25>15>30% for Ta, respectively, as Figure 5. These are in agreement with the experimental results reported by Kant, *et al*., Lajure *etal*., and Murasheva *et al*., [23-25]. At concentrations more than 10% Cu, ionic conductivity of BICUVOX decrease with the encreasing vacancy because of its like-provskite volume is increased

Concentration value of 10% Cu in this study is in good agreement with experimental results reported by Kant, *et al*.[23] which showed that the stable structure of BICUVOX is achieved at 10%, which has a grain pattern and uniform in size with adequate porosity compared with the concentration of 15 and 20%. Concentration of 20% Ta also in good agreement with the experimental results reported by S. Lajure, *et al*. which states that the best conductivity for BITAVOX achieved at a concentration of 20% Ta [24]. BIGAVOX has also the highest conductivity at a concentration of 10% Ga for the gamma phase. According to R. Kant, *et al.* BIGAVOX has highest conductivity at 10% for beta phase not gamma phase [26]. While, according to V. Murasheva *at el*. BIGAVOX phase was gamma at 10% Ga with more uniform grain [25].

Propertiy of Transportand Activation Energy of BIMEVOX

Molecular dynamics simulations of $Bi_2VO_{5.5}$ starting with geometry optimization of the supercell (4×4×4) of $Bi_2VO_{5,5}$ using DLPOLY. In the perovskite layers of the supercell $Bi_2VO_{5.5}$, coordinations of V-O were 4 and 6 that arranged alternately between the bismuth layers (figure 6a). Coordination 4 of V-O (figure 6c) is square planar and the coordination 6 is regular octahedral (Figure 6). Since the super structure is optimized, the ions were distorted in layers of bismuth and perovskite layer as shown in figure 36d. The square planar of V-O turn into tetrahedral coordination (Figure 6f) and the octahedral coordination is distorted (Figure 36e). Therefore, the results of supercell optimization of $Bi_2VO_{5.5}$ in accordance with the expected structure, which is also very similar to the results of the optimization of the unit cell $Bi_2VO_{5,5}$ using the DFT method.

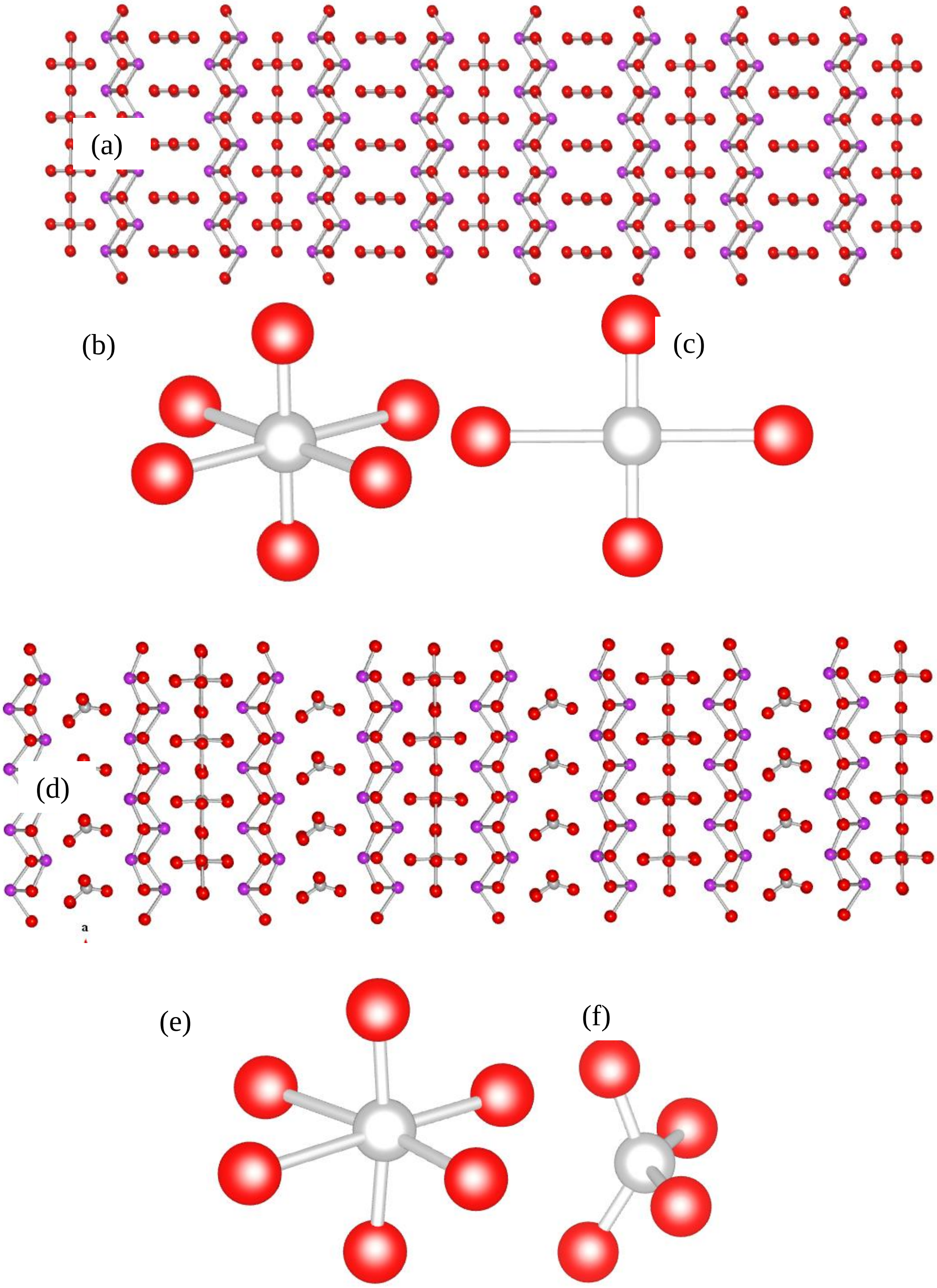


Figure 6 Super cell structure (4×4×4) $Bi_2VO_{5,5}$: (a) before optimization and (d) afteroptimization using DLPOLY code. In the perovskite-like layer, flat rectangular coordination (c) of the V-O has been changed into tetrahedral coordination (f), and the regular octahedral coordination (b) experienced a distorted octahedral coordination (e). In an optimized structure, the ions in the bismuth layer are also distorted.

The successful optimization of the $Bi_2VO_{5.5}$ supercell using DLPOLY has proven that this works well and the short range potential of Buckingham between ions were also correct. Therefore, DLPOLY can be used to perform geometry optimization and molecular dynamics simulations of $Bi_2VO_{5.5}$. Furthermore, the transport properties (through molecular dynamics simulations) of $Bi_2VO_{5.5}$ studied by creating a supercell structure with VO coordinationswere coordination mixtures of tetrahedral, coordination five, and octahedral. The coordination mixtures were representative to show transport properties of the $Bi_2VO_{5.5}$compound.

Molecular dynamics (MD) simulation werecarried out on γ-$Bi_2VO_{5.5}$ and BIMEVOX that were predicted easiest migration of oxygen ions as atomistic simulation results above, namely $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$, $Bi_2Ga_{0.1}V_{0.9}O_{5.4}$, and $Bi_2Ta_{0.2}V_{0.8}O_{5,5}$. Before MD simulation, the supercellsof γ-$Bi_2VO_{5,5}$ and BIMEVOX were optimized first. The optimized structure was controlled at several temperatures to determine the properties of ion transport, such as Mean Square Displacement (MSD) and activation energy. MSD was defined by the formula:

$$\mathrm{MSD}_{\beta}(\mathrm{t}) = \frac{1}{N}\sum_{i=1}^{N}\left[r_i(\mathrm{t}) - r_i(0)\right]^2 \qquad (2)$$

where r_i(t) was the position of ion *i* at time *t*. In a perfect lattice, MSD of component ions usually ranges from the average value. Meanwhile, in the defect lattice there were mobile ions, such as O^{2-} in γ -$Bi_2VO_{5.5}$, where MSD increases over time. Figure 7 shows the MSD data of the γ-$Bi_2VO_{5.5}$ plotted as a function of time at temperatures of 500, 700 and 1100 K.This shown that there were migrating oxide ions, where the temperature rise was followed by an increase in diffusion of oxide ion.

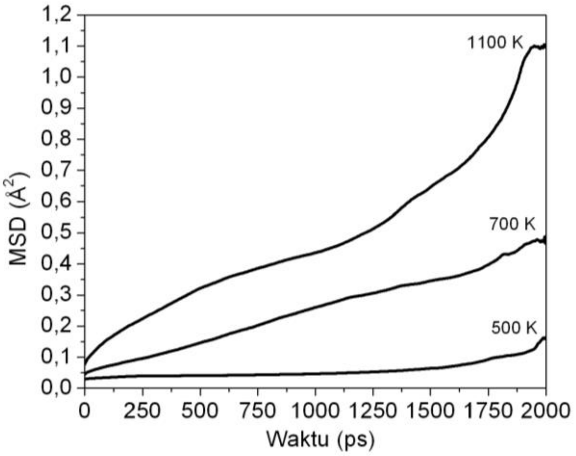


Figure 7 MSD of the oxide ions of γ-$Bi_2VO_{5,5}$at temperatures of 500, 700, and 1100 K. The MSD receives an increase in temperature, which indicates that the diffusion of oxide ions also increases.

From theplot of slope MSD can be determined the diffusion coefficient (D_β) using correlation:

$$MSD_\beta(t) = 6D_\beta(t) - MSD_\beta(0) \quad (3)$$

where $MSD_\beta(0)$ was an atomic vibration factor arising from ion vibrations. The calculation of diffusion coefficient at the three temperatures specified above in Figure 8. From the calculation can be evaluated for activation of ion migration using Arrhenius relationship.

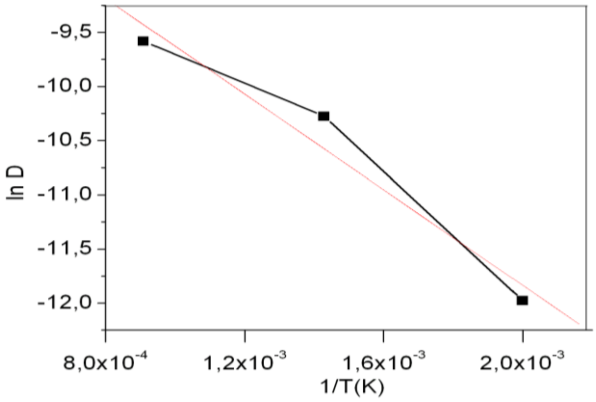


Figure 8. Plot ln D vs 1 / T for oxide ions of γ-$Bi_2VO_{5,5}$.

Based on the Arrhenius plot (ln D vs 1 / T) above, the activation energy obtained is 0.19 eV. This value was a value commonly found in experiments as reported by Joubert et al. [8]

MSD of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ increases with increasing temperature as shown in Figure 9. This indicated that the diffusion of oxide ions increases with increasing temperature. At a temperature of 500, 773 and 823 K, the MSD plot rises to a straight line compared to the MSD plot at 873 K. At 873 K, the oxide ion migration rises rapidly to the timestep 160 ps, then the migration rises slowly to 480 ps, as shown in MSD with lines that are not straight (curved). At the timestep 160-480 ps, the migration of oxide ions was estimated to pass through the obstruction area. This kind of thing is observed in the migration of sodium ions of zeolites [28].

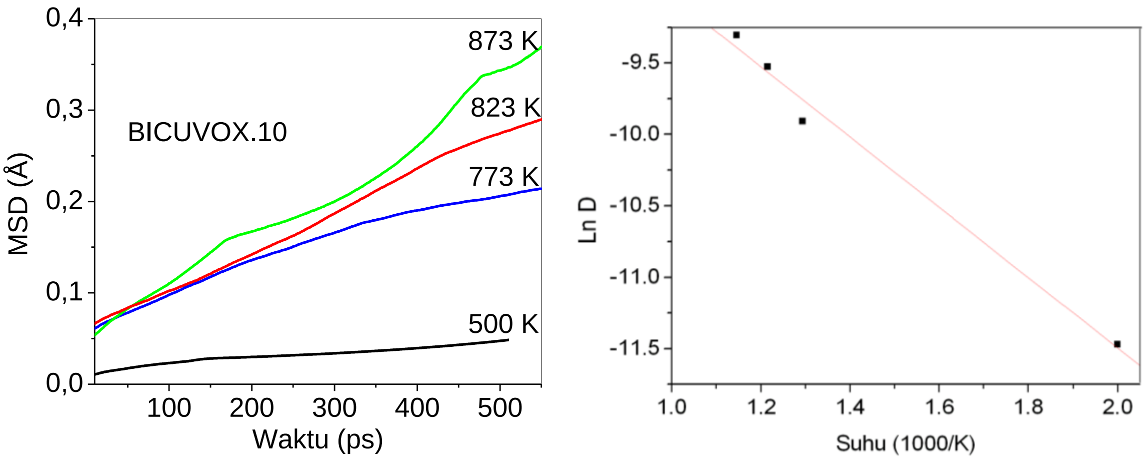


Figure. 9 MSD dan Plot of ln D vs 1/T of oxide ion of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$.

The diffusion coefficient of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ at some temperatures was shown in Figure 7. Based on this graph, the ion activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ was 0,21 eV. This energy value was in accordance with the results of experiments reported by Guillodo *et al*. (2001), but different from those reported by Krok *et al.* (1992) and Simner *et al*. (1997) as shown in Table 2. This difference can be caused by different synthesis methods.

Table 2 The activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ based on the experimental results

Activation Energies (eV)	References
0.48	Krok *et al*. [30]
0.52	Simner *et al*. [31]
0.20	Guillodo *et al*., [29]

The oxide ion MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increases with temperature rise (Figure 8a). Based on the plot of ln (oxide ion diffusion coefficient) on I/T (Figure 10), the activation energy of the calculation result is 0.10 eV. Ion oxide MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increased with increase in temperature. Based on the plot of ln (oxide ion diffusion coefficient) versus I/T, the activation energy was 0.10 eV.

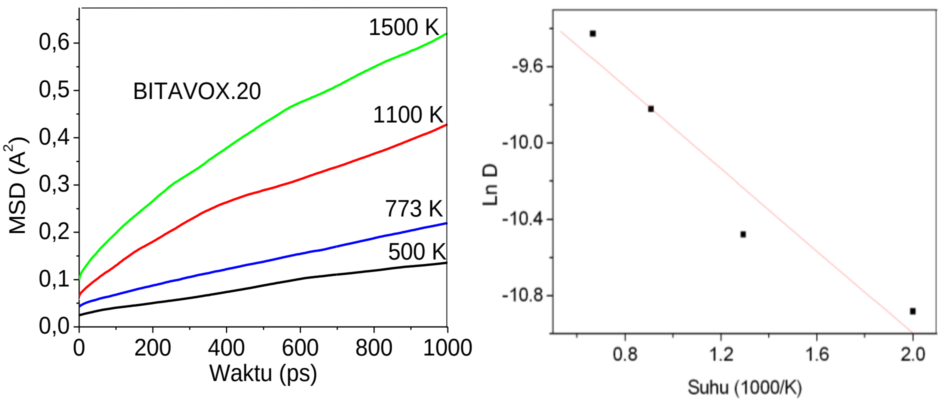


Figure 8. Oxide ion MSD and ln D vs I/T plot of $Bi_2Ta_{0,2}V_{0,8}O_{5,5}$

This activation energy was smaller than the activation energy calculated from γ-$Bi_2VO_{5.5}$ and $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$. This indicated that the conductivity of the $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ was greater than the conductivity of the two types of compound.

CONCLUSIONS

Computational simulation of ionic conductivity of BIMEVOX and γ-$Bi_2VO_{5.5}$ performed using DFT, Mott-Littleton method, and molecular dynamic simualtion. The obtained enthalpy for γ-$Bi_2VO_{5.5}$ close to experimental results. Defect simulation using Mott-Littleton method showed 10% Cu^{2+}, 10% Ga^{3+}, and 20% Ta^{5+} where highest ionic conductivity was in good agreement with the experiment results.The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME= Cu and Ta close to experimental values. The addition of oxygen vacancy at γ-$Bi_2VO_{5.5}$ due to doping with aliovalent dopants, such as Cu and Ga, causes disordering polyhedral in the vanadate layer where oxygen ion migration takes place. In contrast, ordering polyhedral due to the inclusion of isovalent dopants such as Ta causes easier ion migration. To synthesize BIMEVOX compounds which are expected to have high ion conductivity, the concentrations of aliovalent and aliovalent dopants are 10% and 20%, respectively.

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HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): MODELING AND COMPUTATIONAL SIMULATION

ABSTRACT

BIMEVOX had potential to play an important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, oxide ion migrations of γ-$Bi_2VO_{5.5}$ and BIMEVOX were simulated using density function theory (DFT), Mott-Littleton method and molecular dynamic simulation. In γ-$Bi_2VO_{5.5}$, there were oxygen vacancies at the equatorial position in the vanadate layers. These vacancies could facilitate oxide ions migration. The Enthalpy of the oxide migration for γ-$Bi_2VO_{5.5}$based on DFT calculation was 0.38 eV, which was in a good agreement with experimental results. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with Cu^{2+}, Ga^{3+}, and Ta^{5+}. Defect simulation results using the Mott-Littleton method showed that the total maximum energies of region II were achieved at concentrations of 10, 10, and 20%, respectively for Cu^{2+}, Ga^{3+}, and Ta^{5+}. The calculated concentration of Cu^{2+}, Ga^{3+}, and Ta^{5+}were in a good agreement with those of experiment results, where the highest ionic conductivity obtained. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME= Cu and Ta) respectively were 0.19, 0.21, and 0.10 eV, close to experimental values.

Keywords: simulation, defect, γ-$Bi_2VO_{5.5}$ and BIMEVOX, ionic migration.

INTRODUCTION

Solid electrolyte materials with high oxide ion conductivity intensively investigated in order to have solid oxide fuel cell (SOFC). One of oxide materials that had high oxide ion conductivity and potential application was $Bi_2V_{1-x}Me_xO_{5.5-\sigma}$ (BIMEVOX) where ME was dopant [1-3]. Dopant at a certain concentration play an important role in improving the ease of oxygen ions migration of $Bi_2VO_{5.5}$ [4-5]. Therefore, in addition to the migration path of oxygen ions, the search for a type of dopant with a certain concentration was needed to obtain BIMEVOX with high conductivity. Computational simulation method could be conducted first to predict the ease of ion migration.

BIMEVOX was family of oxides derived from $Bi_2VO_{5.5}$ and obtained by doping into the vanadium site of $Bi_2VO_{5.5}$ by aliovalent or isovalent metal cations (ME). The structure of $Bi_2VO_{5.5}$ could be derived from Bi_2MoO_6 and δ-Bi_2MoO_6 by formation of oxygen vacancies in the metal oxygen layers; thus the compound can be formulated as $(Bi_2O_2)(VO_{3.5}\square_{0.5})$, where $\square$ was corresponding to the intrinsic oxygen vacancies [6, 7].

The $Bi_2VO_{5.5}$ goes to several structural transformations and known had several polymorphs, but essentially there were only three main polymorphs, namely α, β, and γ-$Bi_2VO_{5.5}$ with the transformations: $\alpha \rightarrow \beta$ at 720 K and $\beta \rightarrow \gamma$ at 840 K. The structures of α and β-phases were more ordered, larger in unit cell and had lower conductivity. At the high temperature, γ-phase was formed and had conductivity of 0.2 Scm^{-1} at 943 K [8]. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with other metal cations (ME) [9-10]. The substitution do not only stabilize the structure but also increase ionic conductivity due to the creation of vacancies [11]. Therefore, the computational simulation carried out in this study was the gamma phase of $Bi_2VO_{5.5}$ and BIMEVOX (ME = Cu^{2+}, Ga^{3+} and Ta^{5+}).

The experimental results of BIMEVOX compounds showed the contribution of electrons that affected BIMEVOX conductivity [12]. Moreover, the texture of compounds, surface conditions, pore existence, and the presence of impurities affect ionic conductivity. Single phase of BITAVOX could not be obtained by synthesis [13]. Dereerper *et al.* reported that BITAVOX conductivy increase with the increase in Ta dopant concentration. BIGAVOX had a smaller conductivity due to the contribution of electron conductivity [12]. Therefore, the single phase of the gamma-$Bi_2VO_{5.5}$ and BIMEVOX (Cu^{2+}, Ga^{3+} and Ta^{5+}) through computational modeling and simulation was important to be conducted to predict the possibility of ease of migration of oxygen ions without the presence of electron conductivity.

Experimental studies on the oxide ionic conductivity of BIMEVOX have been reported, elsewhere [14]. However, the experimental study could not reveal the detail of the mechanism of oxide ioni conductivity and role of dopant in the BIMEVOX on the structural properties. Computational studies could be used to study many material properties efficiently in order to save time and cost as well as to provide more detail mechanism in the atomic level. Some computation study on the layered structure of Aurivillius phases similar to BIMEVOX has been carried out and reported [15, 16]. It could reveal defect energies and maximum dopant concentrations in Aurivillius as ferroelectric material. From our best knowledge, the computational study on BIMEVOX was not reported yet.

Here, we report the computational study on BIMEVOX and its parent structure that cover trajectory of ionic oxide in γ-$Bi_2VO_{5.5}$ and defect energy of BIMEVOX. The study was aimed to investigate the oxide ion pathways that were possible in the V^{5+} coordination environments of γ-$Bi_2VO_{5.5}$ as well as to predict dopant concentrations of Cu^{2+}, Ga^{3+} and Ta^{5+}

that give the higher ionic conductivity. Subsequently, transport properties and activation energy of migration of oxygen ions of parent compound and BIMEVOX (ME = $Cu^{2+}$and Ta^{5+}) which were predicted to have the highest ionic conductivity were simulated using the molecular dynamics method. Those dopants were selected because of its ionic radius close to ionic radius of V^{5+}.This mean that the dopant with ionic radius close to the V^{5+} radius could enhance the conductivity [17].

METHODS

Enthapy of Oxide Ion Migration

The enthalpies of oxide ion migration of γ-$Bi_2VO_{5.5}$ were calculated by using computational simulation method that is based on density functional theory (DFT). This simulation used CASTEP code of Material Studio Modeling from Accerys, series number 3.2.00, in Politecnico di Torino [18]. Methodology for electronic structure calculations in CASTEP is as follows: set of one-electron Schrodinger (Kohn-Sham) equations are solved using the plane-wave pseudo potential approach. The wave functions are expanded in a plane wave basis set defined by use of periodic boundary condition and Bloch's Theorem. The electron-ion potential is described by means of *ab initio* pseudo potentials within both norm-conserving and ultrasoft formulations. Direct energy minimization schemes are used to obtain self-consistently, the electronic wave functions and its corresponding charge density. Lattice optimisation is initially performed using exchange–correlation energy functions of Perdew–Burke–Ernzerhof (GGA-PBE). Structural optimisation was implemented to determine the best functional approximation to perform in examining the enthalpy of γ-$Bi_2VO_{5.5}$ at various oxygen positions of the tetragonal vanadate layer. A k-point grid of 1×1×1 generated using the Monkhorst–Pack method for Brillouin zone sampling with an energy cut-off of 600 eV.

Atomistic simulation and Molecular Dynamic

The main samples used in this simulation were of two types, namely (i) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with an *I*4/mmm space group as reported by Mairesse et al. [17] and (ii) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with *P*1 space group modified from the first structure. The two structures were then doped with dopant (ME) of Cu, Ga, and Ta to obtain BIMEVOX compounds. In the first structure, the simulation method applied is atomistic simulation using GULP [19]. The simulation aims to calculate defect energy while predicting the ease of migration of oxygen ion in BIMEVOX based on the increase in dopant concentration. While the second structure applied molecular dynamics to determine the property of transport or activation energy of the migration of oxygen ions using the DLPOLY code [20]. Both simulation methods use Buckingham's short range potential defined:

$$\theta_{ij} = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^{6}} \qquad (1)$$

where A_{ij}, ρ_{ij}, and C_{ij} were constant parameters and r_{ij} was the distance between *i* and *j* ions. The first term in equation (1) describes short-range repulsion, while the second term shows induced dipole (van der Waals interaction).

Using DL_POLY, different defect concentrations were simulated by creating supercell of 4×4×4 containing dopant concentrations (10% Cu and 20% Ta) and the respective amount of oxygen vacancies. The simulations were carried out for a step time of 0.0002 ps with ensemble of constant temperature and volume (NVT) and algoritma of leap frog that applied on simulation box of 1088 ions.

Defect Energy of BIMEVOX

Calculation of energy defects in atomistic simulations is performed on the average structure of γ-$Bi_2VO_{5.5}$ and BIMEVOX with space group I4/mmm. The energy defect of BIMEVOX was calculated based on Mott-Littleton method which divides the crystal lattice in the two regions, namely regions I (inner sphere) and II (outer sphere). Region I is the spherical region surrounding defect, which is clearly in relaxation. Meanwhile, the region II is the outer spherical defect that has relatively weak force, which is interpreted with the quasi-continuum approximation method. In this way, the lattice relaxation can be modelled effectively and also the crystal is not as a simple rigid lattice where the diffusion of ions are occurred. If the force on the region II is small, it can be assumed that the response of ions in this region is pure harmonic. There are two kinds of defects, namely impurity and vacancy defects. Impurity defect with a defect centre of V^{5+} is substituted partially with dopants of Cu^{2+}, Ga^{3+}, and Ta^{5+}, while the defect of oxygen vacancies are intrinsic defect as well as its are created in equatorial position of oxygen, O(3). The concentration of dopants which substitutes V partially was compensated by reduction of concentrations of oxygen, O(3), to neutralize the charge in BIMEVOX structure. Defect energy calculations were performed at concentrations of 5, 10, 15, and 20% for each dopant, except for Ta^{5+} that was also carried out at the concentration of 25 and 30%.

RESULTS AND DISCUSSIONS

Geometry optimization of the parent structure, γ-$Bi_2VO_{5.5}$ was an initial procedure to check the structure stability. The structure of γ-$Bi_2VO_{5.5}$ reported by Mairesse *et al.* [17], tetragonal, space group *I*4/mmm, cell unit dimension, *a* = 3.99176(4), *b* = 3.99176(4), and *c* = 15.4309(3) Å was used as a starting model. The mean V – O octahedron were encaged between eight Bi sites. However, due to the O(2) and O(3) split-sites, it was observed there were several short O – O contacts, these preclude simultaneous occupation of many of these O sites as shown in Figure 1.

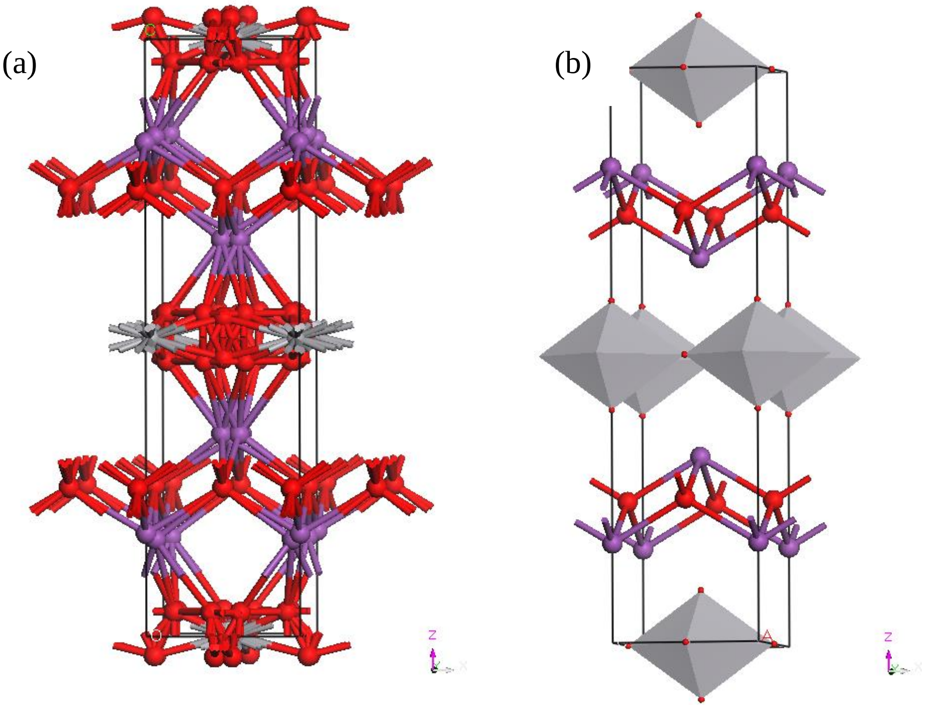

Figure 1. The crystal structuresof $Bi_2VO_{5.5}$,(a) average crystallography structure, and b) the refined structure oxygen vacancies were shown as oxygen atoms..

In fact, the V – O environment which appears as an octahedron squashed along the *c* stacking direction must be viewed as the result of superimposed polyhedral. Indeed, by selecting appropriate O sites among those drawn, the classical O environments of the V cation are easily recognised as octahedron, tetrahedron, trigonal bipyramid, and tetragonal pyramid with interatomic distances compatible with O atomic size [21]. Therefore, the structure, that has high symmetry and contain oxygen vacancy, can be represented using by space group *P1* that had no symmetry, as shown at Figure 2.

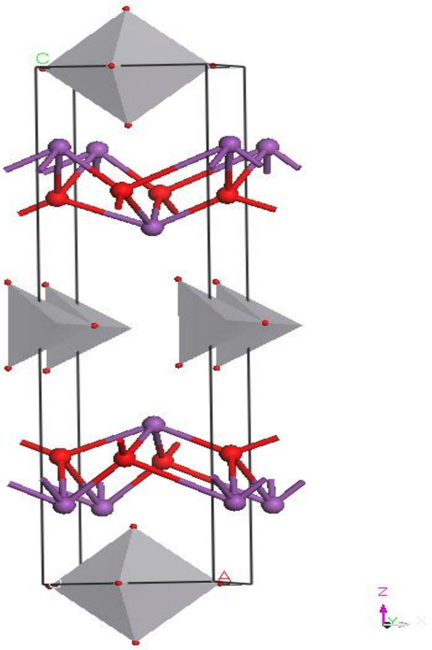

Figure 2. The one possibility of structure that has V - O tetrahedral environment with oxygen vacancy in equatorial site.

The structure in Figure 2 was one of model of structure γ-Bi$_2$VO$_{5.5}$ showing a special vanadium-oxygen anions coordination environment. The structure that is simulated based on DFT indicates that coordination environment of V cations by O(3) and oxygen vancancy are in good agreement with the crystallography site of γ-Bi$_2$VO$_{5.5}$ structure, as depicted in Figures 1*a* and 2.Therefore, the crystal structure (Figure 2) can be used as starting structure to determine activation energy that represent oxygen jump and the easiness of ionic conduction.

Pathway of Oxide Ion Migration of $Bi_2VO_{5.5}$

Oxygen ions which surround the vanadium ions (Figure 3) could be devided into two types, namely apical site, O(2), and equatorial site, O(3). Geometry optimization result of γ-Bi2VO5.5 show that the angle that occupied O(3)-V-vacant O(3) against V was 70 degrees, with O(3)-V bond length of 1.72 Å. Throughout this 70 degrees angle, all the different position of O(3) are optimized to describe oxygen pathways in equatorial site as shown in Figure 3.

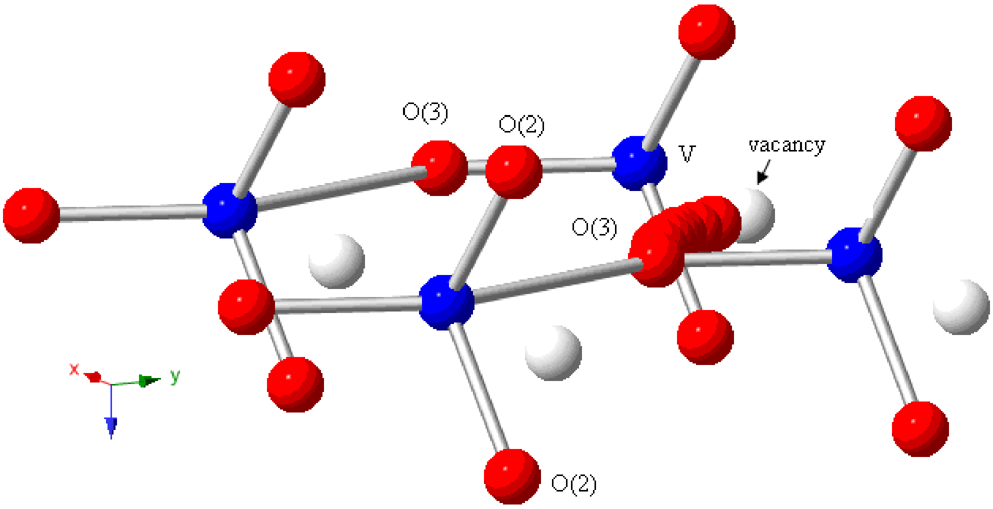

Figure 3. V coordination environments by oxide ions, O(3) equatorial oxygens and O(2) apical oxygens.

Based on result of optimized geometry of γ-$Bi_2VO_{5.5}$, the entalphies of O(3) migration were calculated. The O(3) was moved from one position to the other vacant position. The oxygen position with highest energy, is on the middle between occupied position (initial position) and vacant position, as shown in Figure 4.

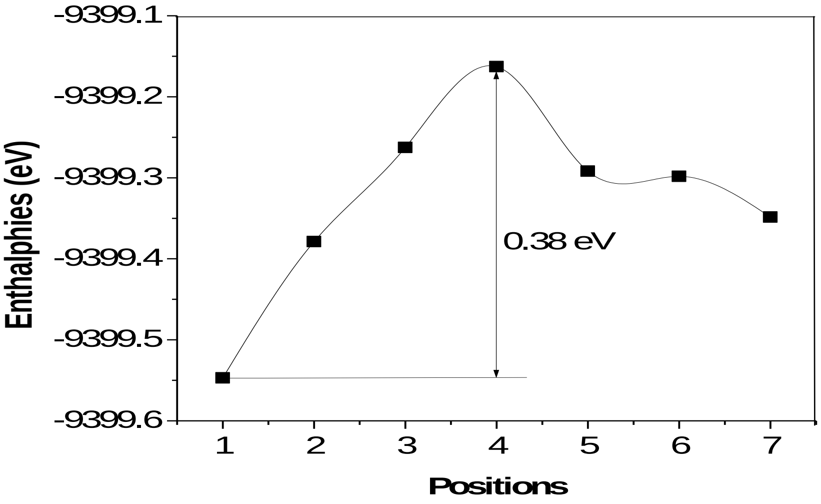

Figure 4. Entalphies of oxygen migration as function of the vacancy position in *γ*-$Bi_2VO_{5.5}$ structure.

The calculated activation energy of oxygen pathway was 0.38 eV and is in good agreement with experiment results as given in Table 1.

Table 1. Activation energies (eV) of oxygen ion motion in *γ*-$Bi_2VO_{5.5}$ based on this simulation work and these obtained from experiment work.

Calculation (this work)	Experiment [ref.]	Description
0.384	0.3427 [14]	Temperature of 773 K, sample obtained from solid state reaction at sintering temperature of 1073 K for 10 and 12 h
	0.35 [15]	Temperature of 873 K, sample obtained from solid state reaction at sintering temperature of 1113 K for 5 h
	0.4 [22]	High temperature, sample obtained from solid state reaction at sintering temperature of 1103 k for 24 h

Defect Energy of BIMEVOX

The calculation of defect energy WAS an important step to treat the lattice relaxation of point defect or migrating ion. In this study, defect energy of BIMEVOX was calculated based on Mott-Littleton method. The number of ions involved in this defect energy calculations were 5,604 ions for region I and 103,016 ions for region II, with each radius was and 37 Å, respectively. Defect energy calculation results were summarized in Figure 5.

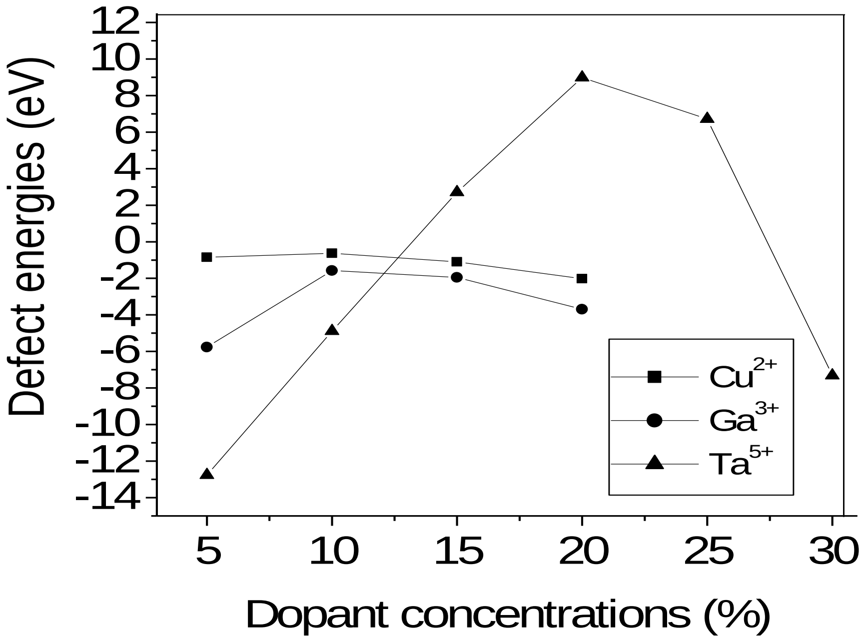

Figure 5. Energy defect in the region II as function of dopant concentration. BIMEVOX structure was expected to more conductive at dopant concentration of 10% Cu, 15% Ga, and 20% Ta.

The results of the defect energy calculations show that the defect energy values of region II varies according to the dopant type and concentration. Energy defect increases up to consentration of 10% for all dopants. However, for Ta^{5+}, defect energy increases with the concentration up to 20%. This was as expected because of Ta is isovalence to V, with valence = +5. Defect energy maximum values were reached at concentrations of 10% for Cu and Ga, and 20% for Ta, with values of -0.63, -1.57 and 8.98 eV, respectively. BICUVOX and BIGAVOX defect energies are more negative at a concentration more than 10%, and the BITAVOX defect energies have a highest negative values at concentrations of 5 and 30% Ta. The negative values of defect energy show that response of ion is pure harmonic and is unstable. Howerer, the BIMEVOXes can be synthesized at the concentrations.

Oxygen vacancies can be varied in accordance with the dopant valence and concentration. The dopant concentration increase the amount of oxygen vacancies in positions O(3). The preference of dopants affect symmetry and connectivity of polyhedral in perovskite-like layer. Consequently, the performance of ionic conductivity is also expected to significantly depend on the defect structure and the effect of trapping on the diffusion pathway of oxygen [14]. Therefore, a stable structure is achieved when each dopant is at a certain concentration. Based on the defect energy values in this work, concentration of dopants that stabilize *γ*-Bi2VO5.5 and were predicted have highest conductivity are 10% for Cu, 10% for Ga, and 20% for Ta. At these concentrations, cation polarisability of dopants are predicted to have achieve maximum value so that facilitate the oxide ion diffusion process in the like-perovskite layers. Again, we predict that sequences of decreasing conductivity of BICUVOX, BIGAVOX, and BITAVOX are 10>15>20% for Cu; 10>15>20% for Ga; and 20>25>15>30% for Ta, respectively, as Figure 5. These are in agreement with the experimental results reported by Kant, *et al*., Lajure *etal*., and Murasheva *et al*., [23-25]. At concentrations more than 10% Cu, ionic conductivity of BICUVOX decrease with the encreasing vacancy because of its like-provskite volume is increased

Concentration value of 10% Cu in this study is in good agreement with experimental results reported by Kant, *et al*. [23] which showed that the stable structure of BICUVOX is achieved at 10%, which has a grain pattern and uniform in size with adequate porosity compared with the concentration of 15 and 20%. Concentration of 20% Ta also in good agreement with the experimental results reported by S. Lajure, *et al*. which states that the best conductivity for BITAVOX achieved at a concentration of 20% Ta [24]. BIGAVOX has also the highest conductivity at a concentration of 10% Ga for the gamma phase. According to R. Kant, *et al.* BIGAVOX has highest conductivity at 10% for beta phase not gamma phase [26]. While, according to V. Murasheva *at el*. BIGAVOX phase was gamma at 10% Ga with more uniform grain [25].

Propertiy of Transportand Activation Energy of BIMEVOX

Molecular dynamics simulations of $Bi_2VO_{5.5}$ starting with geometry optimization of the supercell (4×4×4) of $Bi_2VO_{5,5}$ using DLPOLY. In the perovskite layers of the supercell $Bi_2VO_{5.5}$, coordinations of V-O were 4 and 6 that arranged alternately between the bismuth layers (figure 6a). Coordination 4 of V-O (figure 6c) is square planar and the coordination 6 is regular octahedral (Figure 6). Since the super structure is optimized, the ions were distorted in layers of bismuth and perovskite layer as shown in figure 36d. The square planar of V-O turn into tetrahedral coordination (Figure 6f) and the octahedral coordination is distorted (Figure 36e). Therefore, the results of supercell optimization of $Bi_2VO_{5.5}$ in accordance with the expected structure, which is also very similar to the results of the optimization of the unit cell $Bi_2VO_{5,5}$ using the DFT method.

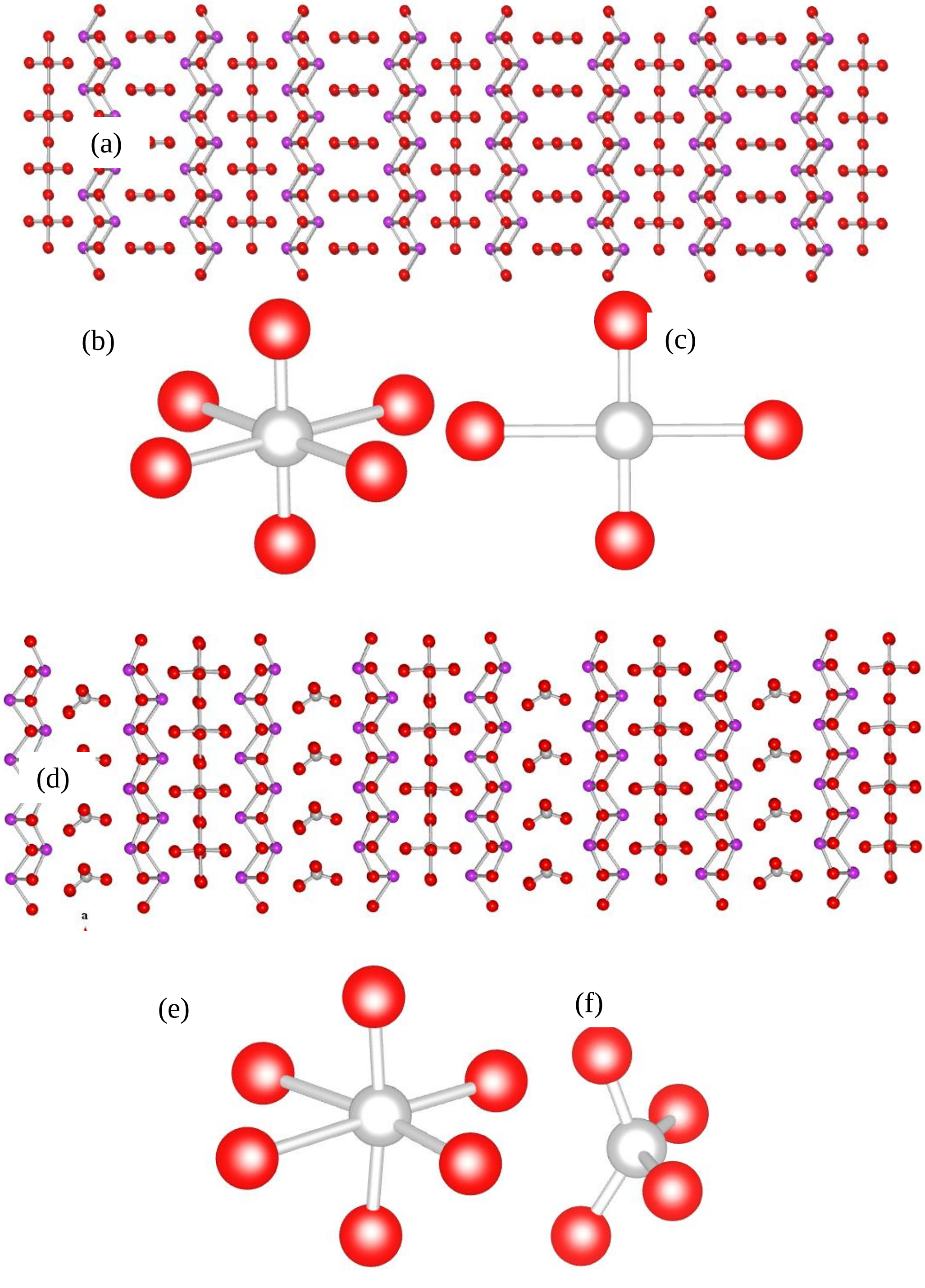

Figure 6 Super cell structure (4×4×4) $Bi_2VO_{5,5}$: (a) before optimization and (d) afteroptimization using DLPOLY code. In the perovskite-like layer, flat rectangular coordination (c) of the V-O has been changed into tetrahedral coordination (f), and the regular octahedral coordination (b) experienced a distorted octahedral coordination (e). In an optimized structure, the ions in the bismuth layer are also distorted.

The successful optimization of the $Bi_2VO_{5.5}$ supercell using DLPOLY has proven that this works well and the short range potential of Buckingham between ions were also correct. Therefore, DLPOLY can be used to perform geometry optimization and molecular dynamics simulations of $Bi_2VO_{5.5}$. Furthermore, the transport properties (through molecular dynamics simulations) of $Bi_2VO_{5.5}$ studied by creating a supercell structure with VO coordinations were coordination mixtures of tetrahedral, coordination five, and octahedral. The coordination mixtures were representative to show transport properties of the $Bi_2VO_{5.5}$compound.

Molecular dynamics (MD) simulation were carried out on γ-$Bi_2VO_{5.5}$ and BIMEVOX that were predicted easiest migration of oxygen ions as atomistic simulation results above, namely $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$, $Bi_2Ga_{0.1}V_{0.9}O_{5.4}$, and $Bi_2Ta_{0.2}V_{0.8}O_{5,5}$. Before MD simulation, the supercellsof γ-$Bi_2VO_{5,5}$ and BIMEVOX were optimized first. The optimized structure was controlled at several temperatures to determine the properties of ion transport, such as Mean Square Displacement (MSD) and activation energy. MSD was defined by the formula:

$$\mathrm{MSD}_{\beta}(\mathrm{t}) = \frac{1}{N}\sum_{i=1}^{N} \left[r_i(\mathrm{t}) - r_i(0)\right]^2 \tag{2}$$

where r_i(t) was the position of ion *i* at time *t*. In a perfect lattice, MSD of component ions usually ranges from the average value. Meanwhile, in the defect lattice there were mobile ions, such as O^{2-} in γ -$Bi_2VO_{5.5}$, where MSD increases over time. Figure 7 shows the MSD data of the γ-$Bi_2VO_{5.5}$ plotted as a function of time at temperatures of 500, 700 and 1100 K.This shown that there were migrating oxide ions, where the temperature rise was followed by an increase in diffusion of oxide ion.

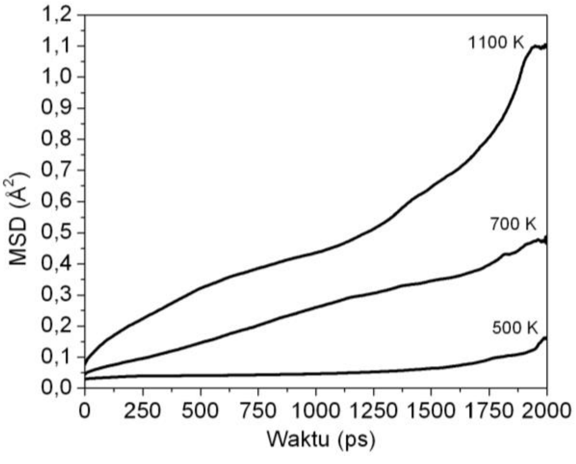

Figure 7 MSD of the oxide ions of *γ*-$Bi_2VO_{5,5}$ at temperatures of 500, 700, and 1100 K. The MSD receives an increase in temperature, which indicates that the diffusion of oxide ions also increases.

From the plot of slope MSD can be determined the diffusion coefficient (D_β) using correlation:

$$\mathrm{MSD}_\beta(t) = 6D_\beta(t) - \mathrm{MSD}_\beta(0) \qquad (3)$$

where $\mathrm{MSD}_\beta(0)$ was an atomic vibration factor arising from ion vibrations. The calculation of diffusion coefficient at the three temperatures specified above in Figure 8. From the calculation can be evaluated for activation of ion migration using Arrhenius relationship.

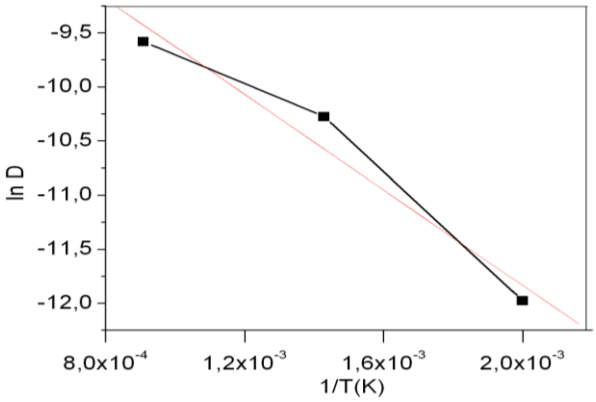

Figure 8. Plot ln D vs 1 / T for oxide ions of γ-$Bi_2VO_{5,5}$.

Based on the Arrhenius plot (ln D vs 1 / T) above, the activation energy obtained is 0.19 eV. This value was a value commonly found in experiments as reported by Joubert et al. [8]

MSD of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ increases with increasing temperature as shown in Figure 9. This indicated that the diffusion of oxide ions increases with increasing temperature. At a temperature of 500, 773 and 823 K, the MSD plot rises to a straight line compared to the MSD plot at 873 K. At 873 K, the oxide ion migration rises rapidly to the timestep 160 ps, then the migration rises slowly to 480 ps, as shown in MSD with lines that are not straight (curved). At the timestep 160-480 ps, the migration of oxide ions was estimated to pass through the obstruction area. This kind of thing is observed in the migration of sodium ions of zeolites [28].

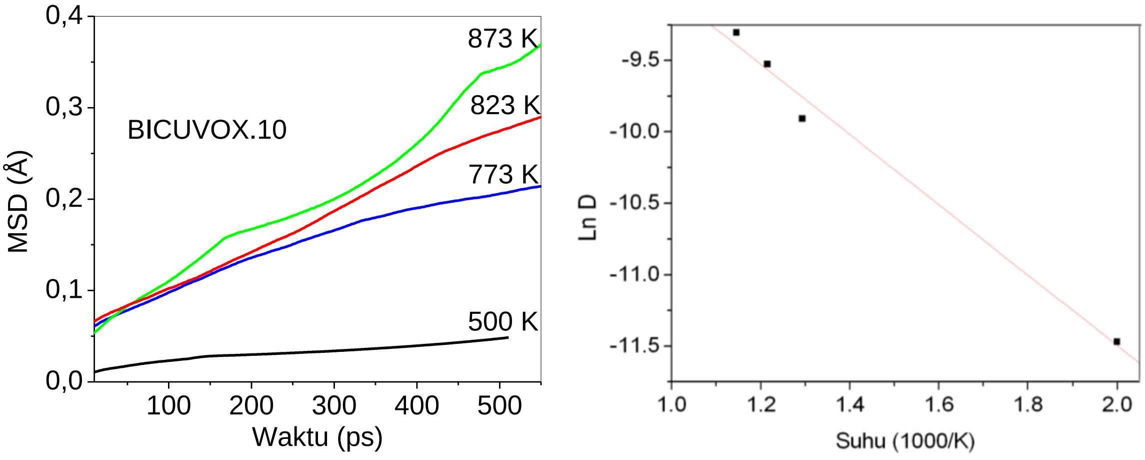

Figure. 9 MSD dan Plot of ln D vs 1/T of oxide ion of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$.

The diffusion coefficient of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ at some temperatures was shown in Figure 7. Based on this graph, the ion activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ was 0,21 eV. This energy value was in accordance with the results of experiments reported by Guillodo *et al*. (2001), but different from those reported by Krok *et al.* (1992) and Simner *et al*. (1997) as shown in Table 2. This difference can be caused by different synthesis methods.

Table 2 The activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ based on the experimental results

Activation Energies (eV)	References
0.48	Krok *et al*. [30]
0.52	Simner *et al*. [31]
0.20	Guillodo *et al*., [29]

The oxide ion MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increases with temperature rise (Figure 8a). Based on the plot of ln (oxide ion diffusion coefficient) on I/T (Figure 10), the activation energy of the calculation result is 0.10 eV. Ion oxide MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increased with increase in temperature. Based on the plot of ln (oxide ion diffusion coefficient) versus I/T, the activation energy was 0.10 eV.

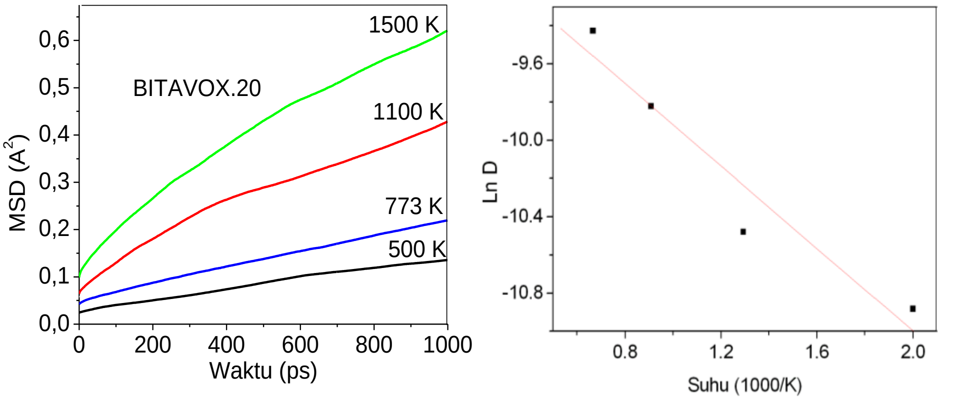

Figure 8. Oxide ion MSD and ln D vs I/T plot of $Bi_2Ta_{0,2}V_{0,8}O_{5,5}$

This activation energy was smaller than the activation energy calculated from γ-$Bi_2VO_{5.5}$ and $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$. This indicated that the conductivity of the $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ was greater than the conductivity of the two types of compound.

The addition of dopant partially to the parent compound (γ-$Bi_2VO_{5.5}$) gives rise to environmental irregularities in the vanadate layer which can inhibit oxygen migration. The irregularity is caused by different size of vanadium (V^{5+} = 0.54 Å) with dopants (Cu^{2+} = 0,73 Å; Ga^{3+} = 0,62 Å; Ta^{5+} = 0,64 Å) and increase of oxygen vacancy due to substitution of V^{5+} partially by Cu^{2+} and Ga^{3+}. On the contrary, doping with Ta^{5+} does not add vacancy because of Ta is isovalent with V. The vacancy can cause strong attraction between vacancies and V/dopant thus increasing the activation energy of the migration of oxygen ion. The non-spherical *d* orbitals of Cu, with the configuration $3d^9$, also cause the vanadium environment to be distorted and can act as a trapping center in process of oxygen ion migration.

Polarization of cations to oxygen ions can facilitate hopping of oxygen ion to vacancy site. This happens because the electron cloud of the oxide ion was pulled by the cation so that the oxide ion was easily moved from the site of lattice. The polarization of the cations to the oxide ions that are getting stronger, will further facilitate the oxide ions to migrate in the crystal lattice. Ta^{5+} cations, theoretically, will be more strong at polarizing oxide ions compared to Ga^{3+} and Cu^{2+} cations, because Ta^{5+} has a greater charge density. As a result, qualitatively it can be predicted that at the same concentration, increase of ionic conductivity is BICUVOX <BIGAVOX <BITAVOX.

CONCLUSIONS

Computational simulation of ionic conductivity of BIMEVOX and γ-$Bi_2VO_{5.5}$ performed using DFT, Mott-Littleton method, and molecular dynamic simualtion. The obtained enthalpy for γ-$Bi_2VO_{5.5}$ close to experimental results. Defect simulation using Mott-Littleton method showed 10% Cu^{2+}, 10% Ga^{3+}, and 20% Ta^{5+} where highest ionic conductivity was in good agreement with the experiment results.The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME= Cu and Ta close to experimental values. The addition of oxygen vacancy at γ-$Bi_2VO_{5.5}$ due to doping with aliovalent dopants, such as Cu and Ga, causes disordering polyhedral in the vanadate layer where oxygen ion migration takes place. In contrast, ordering polyhedral due to the inclusion of isovalent dopants such as Ta causes easier ion migration. To synthesize BIMEVOX compounds which are expected to have high ion conductivity, the concentrations of aliovalent and aliovalent dopants are 10% and 20%, respectively.

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Dear Aulia Sukma Hutama

I have sent the corrected figures to email aulia.sukma.hutama@ugm.ac.id

Thank you very much

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Corrections

Editor
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(1) We find the same reference: Ref. 8 & 27; 11 & 21; 12 & 26.
(2) We edit Ref. 9 for the dissertation chapter, please check.
(3) References and citations for the CASTEP program (ref. [18]),
DL_POLY program [ref. 20] should be like we edited with a red font. Please check.

Author
2019-09-11
03:18 AM

Subject: Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation

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Dear Editor

(1) We find the same reference: Ref. 8 & 27; 11 & 21; 12 & 26.

It has corrected so that no more references were same. We added two references relating to ion conductivity due to doping with aliovalent cations: [8] Rusli, R., Abrahams, I., Patah, A., Prijamboedi, B., & Ismunandar, 2014, Ionic conductivity of Bi 2 Ni x V 1− x O 5.5− 3x/2 (0.1≤ x≤ 0.2) oxides prepared by a low temperature sol-gel route. *In AIP Conference Proceedings* 1589(1), 178-181. [10] La Kilo, A., Umamah, T. S., and Laliyo, L. A. R., 2019, Studi Kestabilan Zirkonia Terdoping Kation Trivalen melalui Pemodelan Atomistik, Jurnal Kimia Sains & Aplikasi, 22(4), 129-135.

(2) We edit Ref. 9 for the dissertation chapter, please check. Because the statement was general about conductivity, it is replaced by other related references, namely [8] Rusli, R., Abrahams, I., Patah, A., Prijamboedi, B., & Ismunandar, 2014, Ionic conductivity of Bi 2 Ni x V 1− x O 5.5− 3x/2 (0.1≤ x≤ 0.2) oxides prepared by a low temperature sol-gel route. *In AIP Conference Proceedings* 1589(1), 178-181.

(3) References and citations for the CASTEP program (ref. [18]),
DL_POLY program [ref. 20] should be like we edited with a red font. Please check.

It corrected according to the how to cite command. While the sentence in the method section not change: This simulation used the CASTEP code of Material Studio Modeling from Accerys, series number 3.2.00, in Politecnico di Torino.: CASTEP is one of the many codes inside studio material. Because this code is paid and bought by Politecnico di Torino, serial nmber and consumer must be included in the research method

Due to changes in references, the reference number on the contents of the manuscript also changes.

Best regards,

Akram

Editor
2019-09-11
02:04 PM

Subject: Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation

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Dear Dr. Akram;

You state in the note:

[10] La Kilo, A., Umamah, T. S., and Laliyo, L. A. R., 2019, Studi Kestabilan Zirkonia Terdoping Kation Trivalen melalui Pemodelan Atomistik, Jurnal Kimia Sains & Aplikasi, 22(4), 129-135.

But in the manuscript:

[11] La Kilo, A., Umamah, T.S., and Laliyo, L.A.R., 2019, Studi kestabilan zirkonia terdoping kation trivalen melalui pemodelan atomistik, *Jurnal Kimia Sains dan Aplikasi*, 22(4), 129–135.

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Regards

Dwi Siswanta

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Dear Dwi Siswanta

Thank you for the good correction.

The following comments are based on the statement above

1. Which one is true?

The correct reference number is [11]

2. We recommend that you do not use the more recent article as a reference for the earlier article.

I replace reference [11] (La Kilo et.,) with the following reference:

[11] Khaerudini, D. S., Guan, G., Zhang, P., Hao, X., Kasai, Y., Kusakabe, K., & Abudula, A., 2014, Structural and conductivity characteristics of Bi4MgxV2− xO11− δ (0⩽ x⩽ 0.3) as solid electrolyte for intermediate temperature SOFC application, *J. Alloys Compd.*, 589, 29-36.

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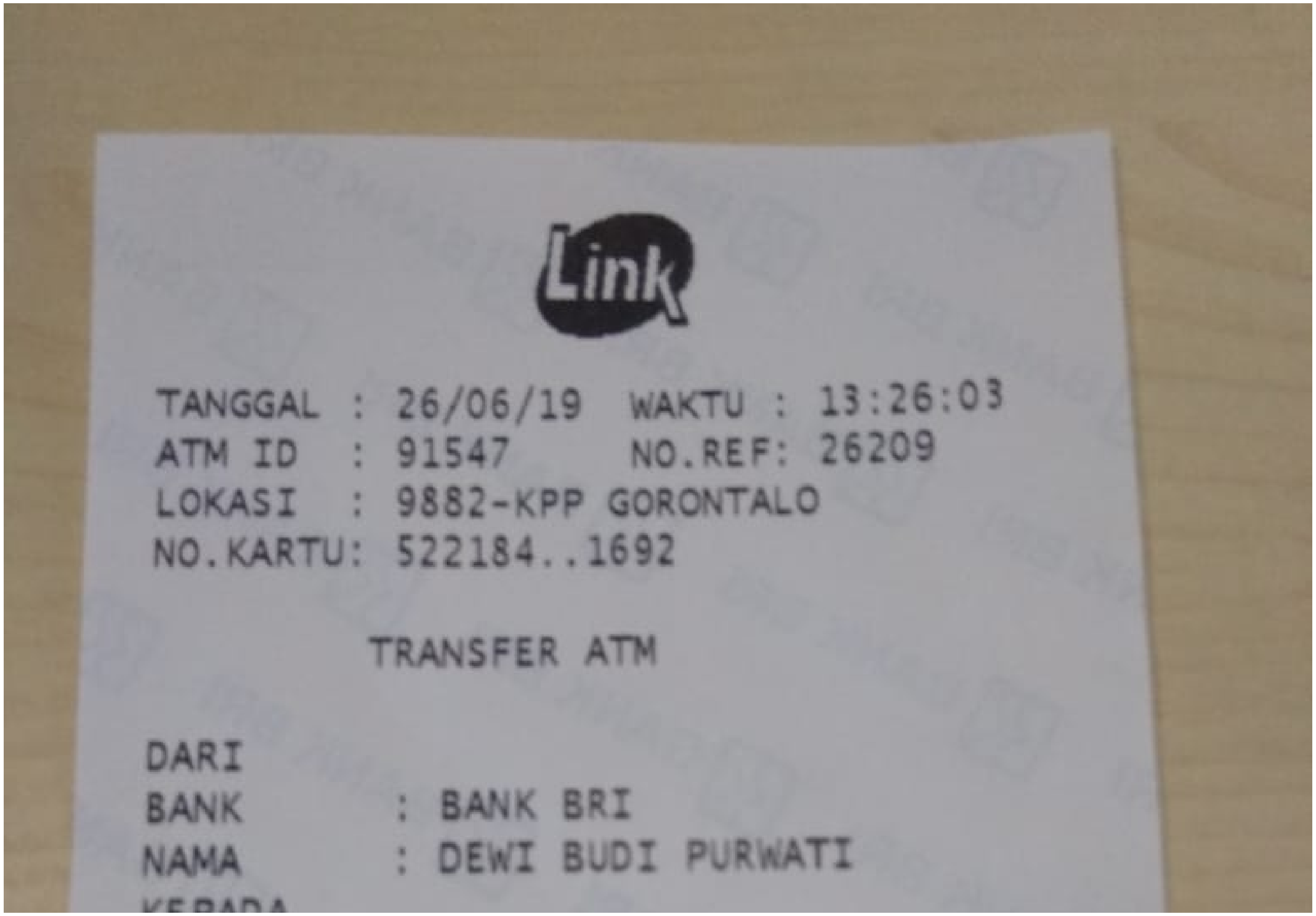

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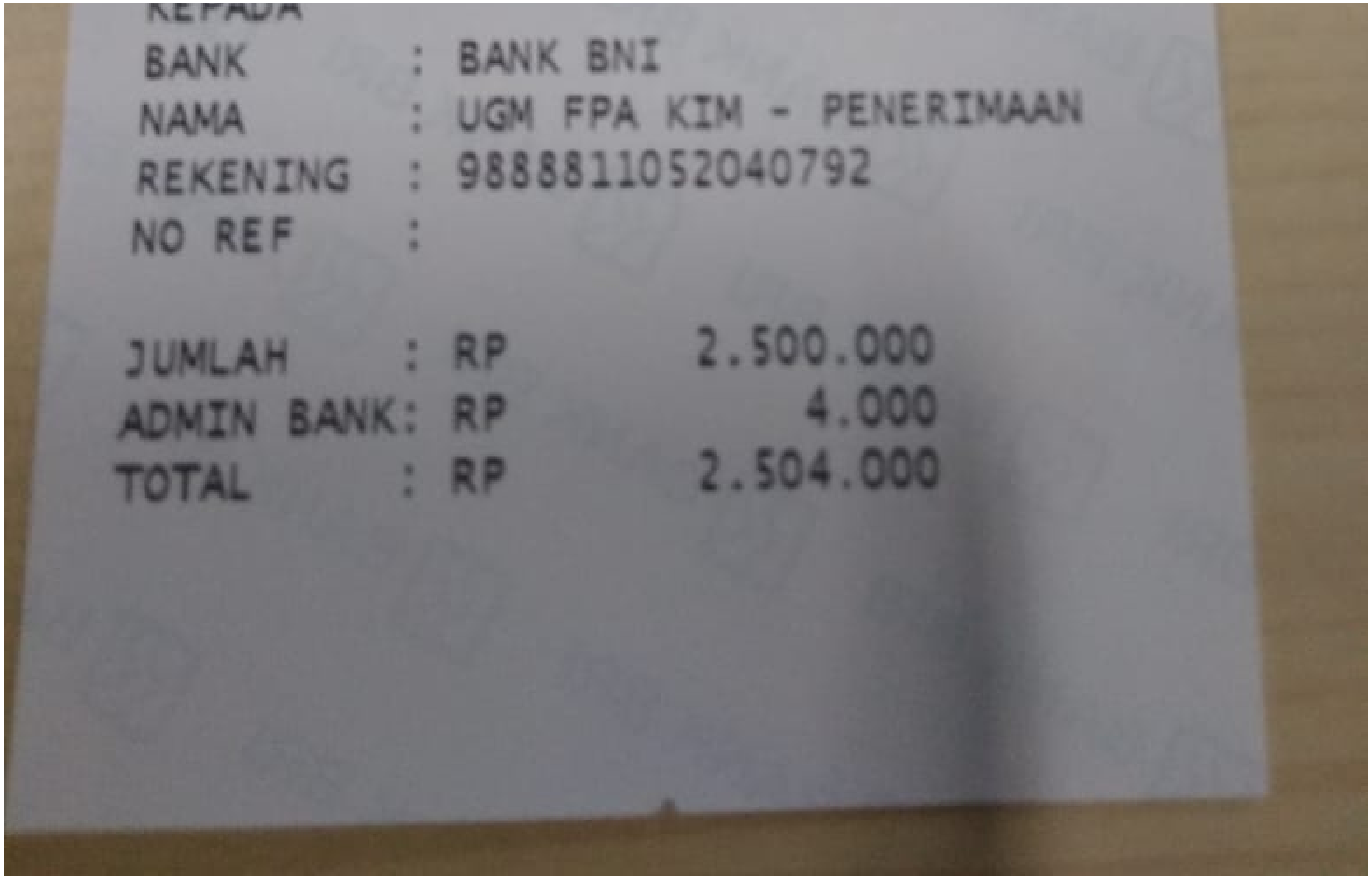

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ABSTRACT
1. CHANGE...
density function theory (DFT)
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density functional theory (DFT)
2. CHANGE...
molecular dynamic simulation
TO...
molecular dynamics simulation
3. CHANGE...
The calculated concentration of Cu2+, Ga3+, and Ta5+ were in a good agreement, where the highest ionic conductivity obtained.
TO...

The calculated concentration of Cu2+, Ga3+, and Ta5+ was in good agreement, where the highest ionic conductivity was obtained.
4. CHANGE...
the activation energies of oxide ion migration in γ-Bi2VO5.5 and BIMEVOX (ME = Cu and Ta) respectively were 0.19, 0.21, and 0.10 eV
TO...
the activation energies of oxide ion migration in γ-Bi2VO5.5 and BIMEVOX (ME = Cu and Ta) were 0.19, 0.21, and 0.10 eV, respectively

INTRODUCTION
5. CHANGE...
BIMEVOX was family of oxides derived
TO...
BIMEVOX was a family of oxides derived
6. CHANGE...
thus the compound can be formulated
TO...
thus, the compound can be formulated
7. CHANGE...
The substitution does not only stabilize the structure but also increase
TO...
The substitution does not only stabilize the structure but also increases
8. CHANGE...
The experimental results of BIMEVOX compounds showed the contribution of electrons that affected BIMEVOX conductivity
TO...
The experimental results of BIMEVOX compounds showed the contribution of electrons that affected BIMEVOX conductivity
9. CHANGE...
BITAVOX conductivy increase
TO...
BITAVOX conductivity increases
10. CHANGE...
have been reported, elsewhere
TO...
have been reported elsewhere
11. CHANGE...
activation energy of migration of oxygen ions of the parent compound and BIMEVOX (ME = Cu2+and Ta5+) which were predicted to have the highest ionic conductivity were simulated
TO...
activation energy of migration of oxygen ions of the parent compound and BIMEVOX (ME = Cu2+and Ta5+), which were predicted to have the highest ionic conductivity were simulated

predicted to have the highest ionic conductivity, were simulated
12. CHANGE...
Those dopants were selected because of its ionic radius
TO...
Those dopants were selected because of their ionic radius

EXPERIMENTAL SECTION

13. CHANGE...
plane-wave pseudo potential approach
TO...
plane-wave pseudopotential approach
14. CHANGE...
Structural optimizations was implemented
TO...
Structural optimizations were implemented
15. CHANGE...
While the second structure applied molecular dynamics to determine
TO...
Meanwhile, the second structure applied molecular dynamics to determine
16. CHANGE...
algorithm of leap frog that applied on simulation box
TO...
algorithm of leapfrog that applied to the simulation box
17. CHANGE...
The concentration of dopants which substitutes V partially was compensated
TO...
The concentration of dopants, which substitutes V partially, was compensated

RESULTS AND DISCUSSION

18. CHANGE...
Geometry optimization of the parent structure, γ-Bi2VO5.5 was an initial procedure
TO...
Geometry optimization of the parent structure, γ-Bi2VO5.5, was an initial procedure
19. CHANGE...
it was observed there were several short O–O contacts, these preclude simultaneous occupation of many of these O sites as shown in Fig. 1.
TO...
it was observed that there were several short O–O contacts; these preclude simultaneous occupation of many of these O sites, as shown in Fig. 1.
20. CHANGE...

the V–O environment which appears as an octahedron squashed along the c stacking direction must be viewed as the result of superimposed polyhedral.

TO...

the V–O environment, which appears as an octahedron squashed along the c stacking direction, must be viewed as the result of a superimposed polyhedral.

21. CHANGE...

The structure in Fig. 2 was one of the models of structure γ-Bi2VO5.5, showing a special

TO...

The structure in Fig. 2 was one of the models of structure γ-Bi2VO5.5 showing a special

22. CHANGE...

Geometry optimization result of a γ-Bi2VO5.5 show that

TO...

Geometry optimization results of a γ-Bi2VO5.5 show that

23. CHANGE...

all the different position

TO...

all the different positions

24. CHANGE...

Defect energy maximum values

TO...

Maximum defect energy values

25. CHANGE...

the response of ion is pure harmonic and unstable

TO...

the response of ion is pure harmonic and is unstable

26. CHANGE...

the concentration of dopants that stabilize γ-Bi2VO5.5 and were predicted have the highest conductivity are

TO...

the concentration of dopants that stabilized γ-Bi2VO5.5 and were predicted to have the highest conductivity are

27. CHANGE...

is predicted to have achieved maximum value so that facilitate the oxide ion diffusion

TO...

is predicted to have achieved maximum value so that it facilitates the oxide ion diffusion

28. CHANGE...

At concentrations more than 10% Cu, the ionic conductivity of BICUVOX decrease with the increasing vacancy because of its like-perovskite volume is increased.

TO...

At concentrations of more than 10% Cu, the ionic conductivity of BICUVOX decreases with the increasing vacancy because its like-perovskite volume increases.

like perovskite volume increases.

29. CHANGE...

which showed that the stable structure of BICUVOX an at 10%, which has a grain pattern and uniform in size with adequate porosity compared with the concentrations of 15 and 20%.

TO...

which showed the stable structure of BICUVOX at 10%, which has a grain pattern and uniform in size with adequate porosity, compared to the concentrations of 15 and 20%.

30. CHANGE...

According to Kant et al. BIGAVOX has the highest conductivity at 10% for a beta phase, not gamma phase

TO...

According to Kant et al., BIGAVOX has the highest conductivity at 10% for a beta phase, not the gamma phase

31. CHANGE...

super structure

TO...

superstructure

32. CHANGE...

From the calculation can be evaluated for activation of ion migration using Arrhenius relationship.

TO...

The calculation can be evaluated for the activation of ion migration using the Arrhenius relationship

33. CHANGE...

two types of compound.

TO...

two types of compounds.

34. CHANGE...

The vacancy can cause the strong attraction between vacancies and V/dopant thus increasing

TO...

The vacancy can cause a strong attraction between vacancies and V/dopants, thus increasing

35. CHANGE...

act as a trapping center in process of oxygen ion migration

TO...

act as a trapping center in the process of oxygen ion migration

36. CHANGE...

the oxide ions that are getting stronger, will further facilitate

TO...

the oxide ions that are getting stronger will further facilitate

CONCLUSION

37. CHANGE...

To synthesize BIMEVOX compounds which are expected

TO...

To synthesize BIMEVOX compounds that are expected

Subject	Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10%
Comments *	

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HIGHEST IONIC CONDUCTIVITY OF BIMEVOX (ME = 10% Cu, 10% Ga, 20%Ta): ~~MODELING AND~~ COMPUTATIONAL MODELING AND SIMULATION

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ABSTRACT

BIMEVOX had the potential to play an important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, oxide ion migrations of γ-$Bi_2VO_{5.5}$ and BIMEVOX were simulated using density function theory (DFT), Mott-Littleton method, and molecular dynamic simulation. In γ-$Bi_2VO_{5.5}$, there were oxygen vacancies at the equatorial position in the vanadate layers. These vacancies could facilitate oxide ions migration. The Enthalpy of the oxide migration for γ-$Bi_2VO_{5.5}$based on DFT calculation was 0.38 eV, which was in a good agreement with experimental results. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with Cu^{2+}, Ga^{3+}, and Ta^{5+}. Defect simulation results using the Mott-Littleton method showed that the total maximum energies of region II were achieved at concentrations of 10, 10, and 20%, respectively for Cu^{2+}, Ga^{3+}, and Ta^{5+}. The calculated concentration of Cu^{2+}, Ga^{3+}, and Ta^{5+}were in a good agreement with those of experiment results, where the highest ionic conductivity obtained. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME= Cu and Ta) respectively were 0.19, 0.21, and 0.10 eV, close to experimental values.

Keywords: simulation;~~,~~ vacancy defect;~~,~~ γ-$Bi_2VO_{5.5}$ and BIMEVOX;~~,~~ ionic migration.

INTRODUCTION

Solid electrolyte materials with high oxide ion conductivity intensively investigated in order to have a solid oxide fuel cell (SOFC). One of the oxide materials that had high oxide ion conductivity and the potential application was $Bi_2V_{1-x}Me_xO_{5.5-\sigma}$ (BIMEVOX) where ME was dopant [1-3]. Dopant at a certain concentration plays an important role in improving the ease of oxygen ions migration of $Bi_2VO_{5.5}$ [4-5]. Therefore, in addition to the migration path of oxygen ions, the search for a type of dopant with a certain concentration was needed to obtain BIMEVOX with high conductivity. Computational simulation method could be conducted first to predict the ease of ion migration.

BIMEVOX was family of oxides derived from $Bi_2VO_{5.5}$ and obtained by doping into the vanadium site of $Bi_2VO_{5.5}$ by aliovalent or isovalent metal cations (ME). The structure of $Bi_2VO_{5.5}$ could be derived from Bi_2MoO_6 and δ-Bi_2MoO_6 by the formation of oxygen vacancies in the metal oxygen layers; thus the compound can be formulated as $(Bi_2O_2)(VO_{3.5}\square_{0.5})$, where □ was corresponding to the intrinsic oxygen vacancies [6, 7].

The $Bi_2VO_{5.5}$ goes to several structural transformations and known had several polymorphs, but essentially there were only three main polymorphs, namely α, β, and γ-$Bi_2VO_{5.5}$ with the transformations: $\alpha \rightarrow \beta$ at 720 K and $\beta \rightarrow \gamma$ at 840 K. The structures of α and β-phases were more ordered, larger in unit cell and had lower conductivity. At the high temperature, γ-phase was formed and had a conductivity of 0.2 Scm^{-1} at 943 K [8]. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with other metal cations (ME) [9-10]. The substitution does not only stabilize the structure but also increase ionic conductivity due to the creation of vacancies [11]. Therefore, the computational simulation carried out in this study was the gamma phase of $Bi_2VO_{5.5}$ and BIMEVOX (ME = Cu^{2+}, $Ga^{3+,}$ and Ta^{5+}).

The experimental results of BIMEVOX compounds showed the contribution of electrons that affected BIMEVOX conductivity [12]. Moreover, the texture of compounds, surface conditions, pore existence, and the presence of impurities affect ionic conductivity. A single phase of BITAVOX could not be obtained by synthesis [13]. Dereerper *et al.* reported that BITAVOX conductivy increase with the increase in Ta dopant concentration. BIGAVOX had a smaller conductivity due to the contribution of electron conductivity [12]. Therefore, the single phase of the gamma-$Bi_2VO_{5.5}$ and BIMEVOX (Cu^{2+}, $Ga^{3+,}$ and Ta^{5+}) through computational modeling and simulation was important to be conducted to predict the possibility of ease of migration of oxygen ions without the presence of electron conductivity.

Experimental studies on the oxide ionic conductivity of BIMEVOX have been reported, elsewhere [14]. However, the experimental study could not reveal the detail of the mechanism of oxide ioni conductivity and role of dopant in the BIMEVOX on the structural properties. Computational studies could be used to study many material properties efficiently in order to save time and cost as well as to provide more detail mechanism at the atomic level. Some computation study on the layered structure of Aurivillius phases similar to BIMEVOX has been carried out and reported [15, 16]. It could reveal defect energies and maximum dopant concentrations in Aurivillius as ferroelectric material. From our best knowledge, the computational study on BIMEVOX was not reported yet.

Here, we report the computational study on BIMEVOX and its parent structure that cover the trajectory of ionic oxide in γ-$Bi_2VO_{5.5}$ and defect energy of BIMEVOX. The study was aimed to investigate the oxide ion pathways that were possible in the V^{5+} coordination environments of γ-$Bi_2VO_{5.5}$ as well as to predict dopant concentrations of Cu^{2+}, $Ga^{3+,}$ and Ta^{5+} that give the higher ionic conductivity. Subsequently, transport properties and activation energy of migration of oxygen ions of the parent compound and BIMEVOX (ME = $Cu^{2+}$and Ta^{5+}) which were predicted to have the highest ionic conductivity were simulated using the molecular dynamics method. Those dopants were selected because of its ionic radius close to the ionic radius of V^{5+}. This means that the dopant with an ionic radius close to the V^{5+} radius could enhance the conductivity [17].

METHODS

Enthapy of Oxide Ion Migration

The enthalpies of oxide ion migration of γ-$Bi_2VO_{5.5}$ were calculated by using computational simulation method that is based on density functional theory (DFT). This simulation used the CASTEP code of Material Studio Modeling from Accerys, series number 3.2.00, in Politecnico di Torino [18]. Methodology for electronic structure calculations in CASTEP is as follows: set of one-electron Schrodinger (Kohn-Sham) equations are solved using the plane-wave pseudo potential approach. The wave functions are expanded in a plane wave basis set defined by the use of periodic boundary condition and Bloch's Theorem. The electron-ion potential is described by means of *ab initio* pseudo potentials within both norm-conserving and ultrasoft formulations. Direct energy minimization schemes are used to obtain self-consistently, the electronic wave functions and its corresponding charge density. Lattice optimisation is initially performed using exchange–correlation energy functions of Perdew–Burke–Ernzerhof (GGA-PBE). Structural optimisation was implemented to determine the best functional approximation to perform in examining the enthalpy of γ-$Bi_2VO_{5.5}$ at various oxygen positions of the tetragonal vanadate layer. A k-point grid of 1×1×1 generated using the Monkhorst–Pack method for Brillouin zone sampling with an energy cut-off of 600 eV.

Atomistic simulation and Molecular Dynamic

The main samples used in this simulation were of two types, namely (i) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with an *I*4/*mmm* space group as reported by Mairesse et al. [17] and (ii) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with *P*1 space group modified from the first structure. The two structures were then doped with a dopant (ME) of Cu, Ga, and Ta to obtain BIMEVOX compounds. In the first structure, the simulation method applied is atomistic simulation using GULP [19]. The simulation aims to calculate defect energy while predicting the ease of migration of oxygen ion in BIMEVOX based on the increase in dopant concentration. While the second structure applied molecular dynamics to determine the property of transport or activation energy

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of the migration of oxygen ions using the DLPOLY code [20]. Both simulation methods use Buckingham's short range potential defined:

$$\theta_{ij} = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^{6}} \qquad (1)$$

where A_{ij}, ρ_{ij}, and C_{ij} were constant parameters and r_{ij} was the distance between *i* and *j* ions. The first term in equation (1) describes short-range repulsion, while the second term shows induced dipole (van der Waals interaction).

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Using DL_POLY, different defect concentrations were simulated by creating supercell of 4×4×4 containing dopant concentrations (10% Cu and 20% Ta) and the respective amount of oxygen vacancies. The simulations were carried out for a step time of 0.0002 ps with an ensemble of constant temperature and volume (NVT) and algoritma of leap frog that applied on simulation box of 1088 ions.

Defect Energy of BIMEVOX

Calculation of energy defects in atomistic simulations is performed on the average structure of γ-$Bi_2VO_{5.5}$ and BIMEVOX with space group *I*4/*mmm*. The energy defect of BIMEVOX was calculated based on Mott-Littleton method which divides the crystal lattice into the two regions, namely regions I (inner sphere) and II (outer sphere). Region I is the spherical region surrounding defect, which is clearly in relaxation. Meanwhile, the region II is the outer spherical defect that has relatively weak force, which is interpreted with the quasi-continuum approximation method. In this way, the lattice relaxation can be modelled effectively and also the crystal is not as a simple rigid lattice where the diffusion of ions occurs. If the force on the region II is small, it can be assumed that the response of ions in this region is pure harmonic. There are two kinds of defects, namely impurity, and vacancy defects. Impurity defect with a defect centre of V^{5+} is substituted partially with dopants of Cu^{2+}, Ga^{3+}, and Ta^{5+}, while the defect of oxygen vacancies are intrinsic defect as well as its being created in equatorial position of oxygen, O(3). The concentration of dopants which substitutes V partially was compensated by a reduction of concentrations of oxygen, O(3), to neutralize the charge in BIMEVOX structure. Defect energy calculations were performed at concentrations of 5, 10, 15, and 20% for each dopant, except for Ta^{5+} that was also carried out at the concentration of 25 and 30%.

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RESULTS AND DISCUSSIONS

Geometry optimization of the parent structure, γ-$Bi_2VO_{5.5}$ was an initial procedure to check the structure stability. The structure of γ-$Bi_2VO_{5.5}$ reported by Mairesse *et al.* [17], tetragonal, space group *I*4/mmm, cell unit dimension, *a* = 3.99176(4), *b* = 3.99176(4), and *c* = 15.4309(3) Å was used as a starting model. The mean V – O octahedron was encaged between eight Bi sites. However, due to the O(2) and O(3) split-sites, it was observed there were several short O – O contacts, these preclude simultaneous occupation of many of these O sites as shown in Figure 1.

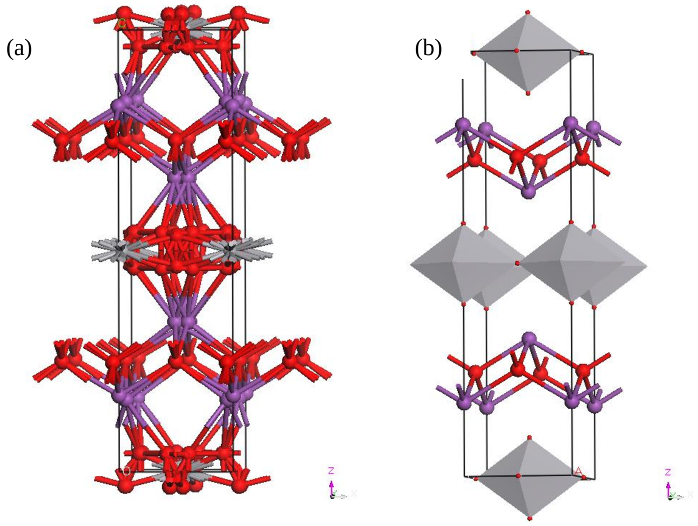

Figure 1. The crystal structuresof Bi$_2$VO$_{5.5}$,(a) average crystallography structure, and b) the refined structure oxygen vacancies were shown as oxygen atoms.

In fact, the V – O environment which appears as an octahedron squashed along the *c* stacking direction must be viewed as the result of superimposed polyhedral. Indeed, by selecting appropriate O sites among those drawn, the classical O environments of the V cation are easily recognised as octahedron, tetrahedron, trigonal bipyramid, and tetragonal pyramid with interatomic distances compatible with O atomic size [21]. Therefore, the structure, that has high symmetry and contains oxygen vacancy, can be represented using by space group *P*1 that had no symmetry, as shown in Figure 2.

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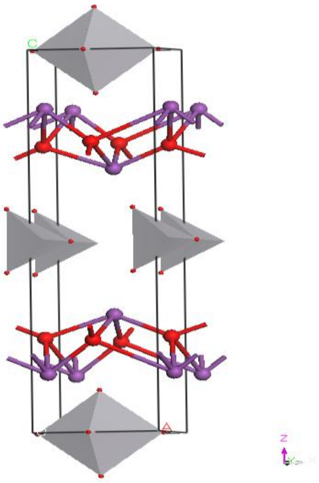

Figure 2. The one possibility of a structure that has V - O tetrahedral environment with oxygen vacancy in the equatorial site.

The structure in Figure 2 was one of the models of structure *γ*-$Bi_2VO_{5.5}$ showing a special vanadium-oxygen anions coordination environment. The structure that is simulated based on DFT indicates that coordination environment of V cations by O(3) and oxygen vancancy are in good agreement with the crystallography site of *γ*-$Bi_2VO_{5.5}$ structure, as depicted in Figures 1*a* and 2.Therefore, the crystal structure (Figure 2) can be used as a starting structure to determine activation energy that represents oxygen jump and the easiness of ionic conduction.

Pathway of Oxide Ion Migration of $Bi_2VO_{5.5}$

Oxygen ions which surround the vanadium ions (Figure 3) could be devided into two types, namely apical site, O(2), and equatorial site, O(3). Geometry optimization result of a *γ*-$Bi_2VO_{5.5}$ show that the angle that occupied O(3)-V-vacant O(3) against V was 70 degrees, with O(3)-V bond length of 1.72 Å. Throughout this 70 degrees angle, all the different position of O(3) are optimized to describe oxygen pathways in the equatorial site as shown in Figure 3.

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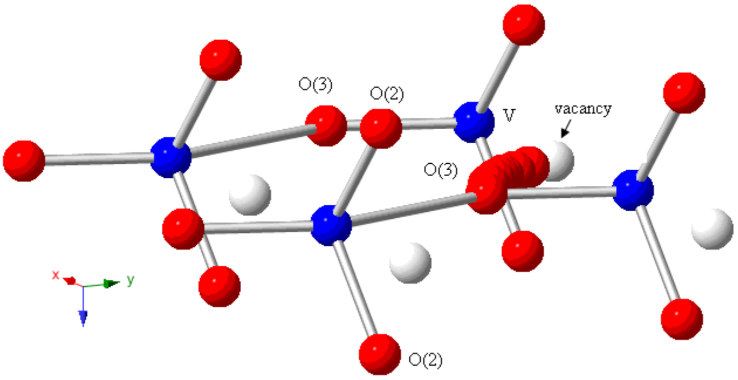

Figure 3. V coordination environments by oxide ions, O(3) equatorial oxygens and O(2) apical oxygens.

Based on the result of the optimized geometry of γ-$Bi_2VO_{5.5}$, the entalphies of O(3) migration were calculated. The O(3) was moved from one position to the other vacant position. The oxygen position with the highest energy, is in the middle between occupied position (initial position) and vacant position, as shown in Figure 4.

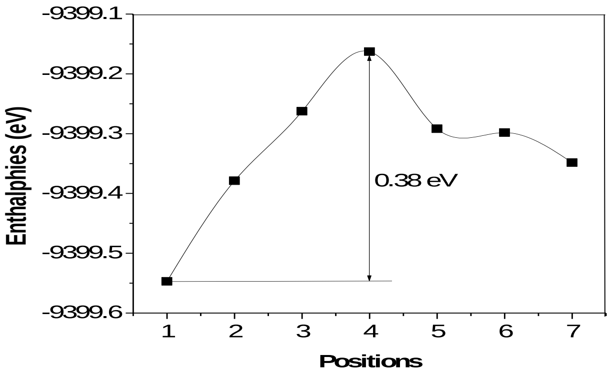

Figure 4. Entalphies of oxygen migration as a function of the vacancy position in the γ-$Bi_2VO_{5.5}$ structure.

The calculated activation energy of oxygen pathway was 0.38 eV and is in good agreement with experiment results as given in Table 1.

Table 1. Activation energies (eV) of oxygen ion motion in γ-$Bi_2VO_{5.5}$ based on this simulation work and these obtained from experiment work.

Calculation (this work)	Experiment [ref.]	Description
0.384	0.3427 [14]	The temperature of 773 K, the sample obtained from a solid state reaction at sintering temperature of 1073 K for 10 and 12 h
	0.35 [15]	The temperature of 873 K, the sample obtained from a solid state reaction at a sintering temperature of 1113 K for 5 h
	0.4 [22]	High temperature, the sample obtained from solid state reaction at sintering temperature of 1103 k for 24 h

Defect Energy of BIMEVOX

The calculation of defect energy was an important step to treat the lattice relaxation of point defect or migrating ion. In this study, the defect energy of BIMEVOX was calculated based on Mott-Littleton method. The number of ions involved in this defect energy calculations was 5,604 ions for the region I and 103,016 ions for region II, with each radius was and 37 Å, respectively. Defect energy calculation results were summarized in Figure 5.

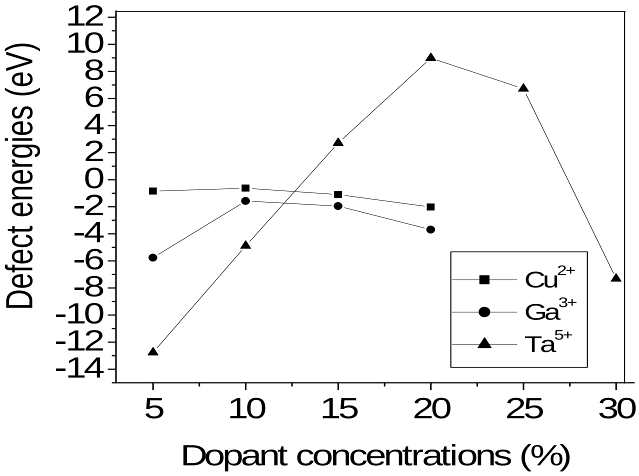

Figure 5. Energy defect in region II as a function of dopant concentration. BIMEVOX structure was expected to more conductive at a dopant concentration of 10% Cu, 15% Ga, and 20% Ta.

The results of the defect energy calculations show that the defect energy values of region II vary according to the dopant type and concentration. Energy defect increases up to conc~~s~~entration of 10% for all dopants. However, for Ta^{5+}, defect energy increases with the concentration of up to 20%. This was as expected because of Ta is isovalence to V, with valence = +5. Defect energy maximum values were reached at concentrations of 10% for Cu and Ga, and 20% for Ta, with values of -0.63, -1.57 and 8.98 eV, respectively. BICUVOX and BIGAVOX defect energies are more negative at a concentration of more than 10%, and the BITAVOX defect energies have the highest negative values at concentrations of 5 and 30% Ta. The negative values of defect energy show that the response of ion is pure harmonic and is unstable. Howerer, the BIMEVOXes can be synthesized at the concentrations.

Oxygen vacancies can be varied in accordance with the dopant valence and concentration. The dopant concentration increases the amount of oxygen vacancies in positions O(3). The preference of dopants affects symmetry and connectivity of polyhedral in the perovskite-like layer. Consequently, the performance of ionic conductivity is also expected to significantly depend on the defect structure and the effect of trapping on the diffusion pathway of oxygen [14]. Therefore, a stable structure is achieved when each dopant is at a certain concentration. Based on the defect energy values in this work, the concentration of dopants that stabilize γ-Bi$_2$VO$_{5.5}$ and were predicted have the highest conductivity are 10% for Cu, 10% for Ga, and 20% for Ta. At these concentrations, cation polarisability of dopants is predicted to have achieved maximum value so that facilitate the oxide ion diffusion process in the like-perovskite layers. Again, we predict that sequences of decreasing conductivity of BICUVOX, BIGAVOX, and BITAVOX are 10>15>20% for Cu; 10>15>20% for Ga; and 20>25>15>30% for Ta, respectively, as Figure 5. These are in agreement with the experimental results reported by Kant, *et al*., Lajure *etal*., and Murasheva *et al*., [23-25]. At concentrations more than 10% Cu, the ionic conductivity of BICUVOX decrease with the encreasing vacancy because of its like-provskite volume is increased

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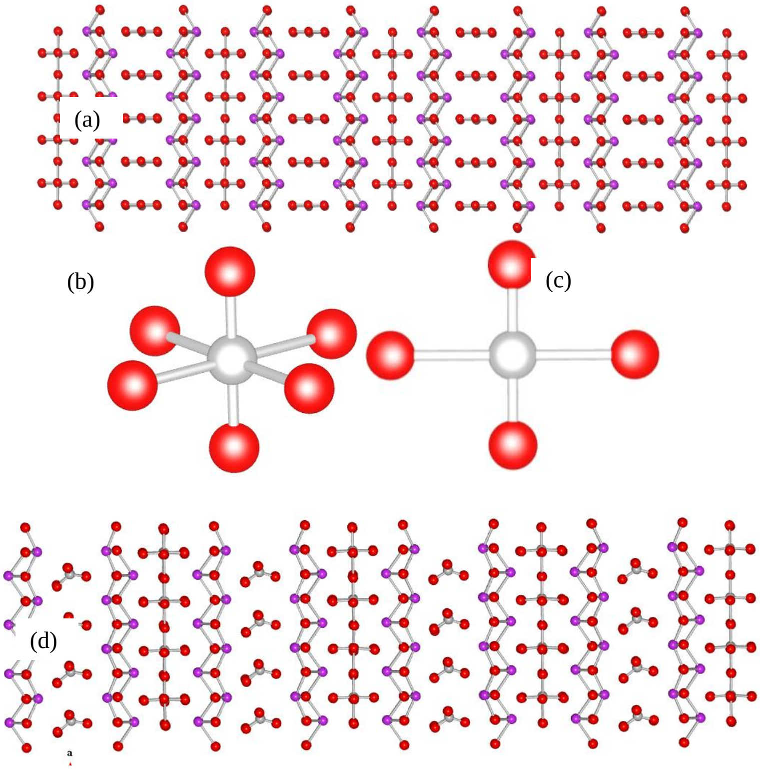
Concentration value of 10% Cu in this study is in good agreement with experimental results reported by Kant, *et al*. [23] which showed that the stable structure of BICUVOX is achieved at 10%, which has a grain pattern and uniform in size with adequate porosity compared with the concentrations of 15 and 20%. Concentration of 20% Ta also in good agreement with the experimental results reported by S. Lajure, *et al*. which states that the best conductivity for BITAVOX achieved at a concentration of 20% Ta [24]. BIGAVOX has also the highest conductivity at a concentration of 10% Ga for the gamma phase. According to R. Kant, *et al.* BIGAVOX has the highest conductivity at 10% for a beta phase, not gamma phase [26]. While according to V. Murasheva *at el*. BIGAVOX phase was gamma at 10% Ga with more uniform grain [25].

Propertiy of Transportand Activation Energy of BIMEVOX

Molecular dynamics simulations of $Bi_2VO_{5.5}$ starting with geometry optimization of the supercell (4×4×4) of $Bi_2VO_{5,5}$ using DLPOLY. In the perovskite layers of the supercell $Bi_2VO_{5.5}$, coordinations of V-O were 4 and 6 that arranged alternately between the bismuth layers (figure 6a). Coordination 4 of V-O (figure 6c) is square planar and the coordination 6 is regular octahedral (Figure 6). Since the super structure is optimized, the ions were distorted in layers of bismuth and perovskite layer as shown in figure 36d. The square planar of V-O turn into tetrahedral coordination (Figure 6f) and the octahedral coordination is distorted (Figure 36e). Therefore, the results of the supercell optimization of $Bi_2VO_{5.5}$ in accordance with the expected structure, which is also very similar to the results of the optimization of the unit cell $Bi_2VO_{5,5}$ using the DFT method.



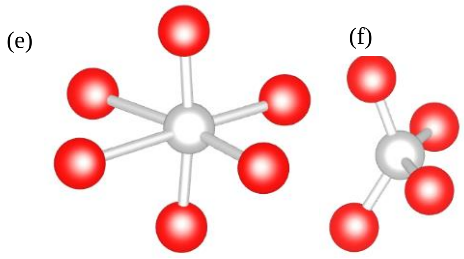


Figure 6. Super cell structure (4×4×4) $Bi_2VO_{5,5}$: (a) before optimization and (d) afteroptimization using DLPOLY code. In the perovskite-like layer, flat rectangular coordination (c) of the V-O has been changed into tetrahedral coordination (f), and the regular octahedral coordination (b) experienced distorted octahedral coordination (e). In an optimized structure, the ions in the bismuth layer are also distorted.

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The successful optimization of the $Bi_2VO_{5.5}$ supercell using DLPOLY has proven that this works well and the short range potential of Buckingham between ions was also correct. Therefore, DLPOLY can be used to perform geometry optimization and molecular dynamics simulations of $Bi_2VO_{5.5}$. Furthermore, the transport properties (through molecular dynamics simulations) of $Bi_2VO_{5.5}$ studied by creating a supercell structure with VO coordinations were coordination mixtures of tetrahedral, coordination five, and octahedral. The coordination mixtures were representative to show the transport properties of the $Bi_2VO_{5.5}$ compound.

Molecular dynamics (MD) simulation were carried out on γ-$Bi_2VO_{5.5}$ and BIMEVOX that were predicted easiest migration of oxygen ions as atomistic simulation results above, namely $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$, $Bi_2Ga_{0.1}V_{0.9}O_{5.4}$, and $Bi_2Ta_{0.2}V_{0.8}O_{5,5}$. Before the MD simulation, the supercells of γ-$Bi_2VO_{5,5}$ and BIMEVOX were optimized first. The optimized structure was controlled at several temperatures to determine the properties of ion transport, such as mean square displacement (MSD) and activation energy. MSD was defined by the formula:

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$$\mathrm{MSD}_{\beta}(\mathrm{t}) = \frac{1}{N}\sum_{i=1}^{N}\left[r_i(\mathrm{t}) - r_i(0)\right]^2 \qquad (2)$$

where r_i(t) was the position of ion *i* at time *t*. In a perfect lattice, MSD of component ions usually ranges from the average value. Meanwhile, in the defect lattice, there were mobile ions, such as O^{2-} in γ-$Bi_2VO_{5.5}$, where MSD increases over time. Figure 7 shows the MSD data of the γ-$Bi_2VO_{5.5}$ plotted as a function of time at temperatures of 500, 700 and 1100 K.This shown that there were migrating oxide ions, where the temperature rise was followed by an increase in the diffusion of oxide ion.

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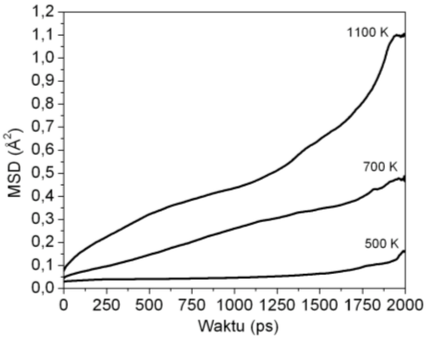

Figure 7. MSD of the oxide ions of γ-$Bi_2VO_{5,5}$ at temperatures of 500, 700, and 1100 K. The MSD receives an increase in temperature, which indicates that the diffusion of oxide ions also increases.

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From the plot of slope MSD can be determined by the diffusion coefficient (D_β) using correlation:

$$MSD_\beta(t) = 6D_\beta(t) - MSD_\beta(0) \quad (3)$$

where $MSD_\beta(0)$ was an atomic vibration factor arising from ion vibrations. The calculation of the diffusion coefficient at the three temperatures specified ~~above~~ in Figure 8. From the calculation can be evaluated for activation of ion migration using Arrhenius relationship.

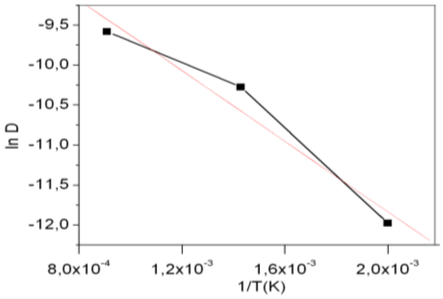

Figure 8. Plot ln D vs 1 / T for oxide ions of γ-$Bi_2VO_{5,5}$.

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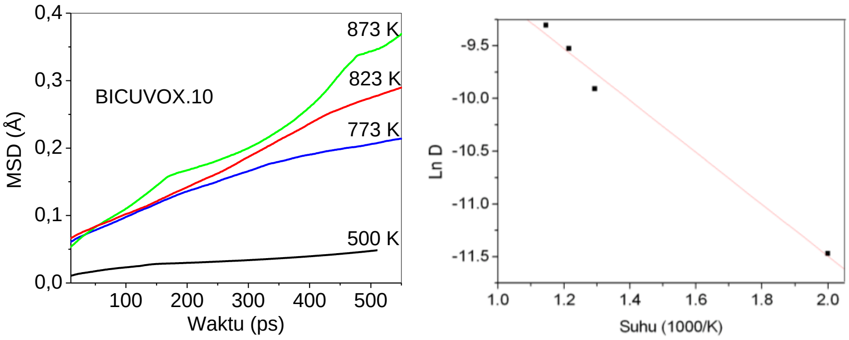
Based on the Arrhenius plot (ln D vs 1 / T) above, the activation energy obtained is 0.19 eV. This value was a value commonly found in experiments as reported by Joubert et al. [8]

MSD of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ increases with increasing temperature as shown in Figure 9. This indicated that the diffusion of oxide ions increases with increasing temperature. At a temperature of 500, 773 and 823 K, the MSD plot rises to a straight line compared to the MSD plot at 873 K. At 873 K, the oxide ion migration rises rapidly to the timestep 160 ps, then the migration rises slowly to 480 ps, as shown in MSD with lines that are not straight (curved). At the timestep 160-480 ps, the migration of oxide ions was estimated to pass through the obstruction area. This kind of thing is observed in the migration of sodium ions of zeolites [28].



Figure~~.~~ 9. MSD dan Plot of ln D vs 1/T of oxide ion of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$.

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The diffusion coefficient of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ at some temperatures was shown in Figure ~~7~~9. Based on this graph, the ion activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ was 0,21 eV. This energy value was in accordance with the results of experiments reported by Guillodo *et al*. (2001), but different from those reported by Krok *et al.* (1992) and Simner *et al*. (1997) as shown in Table 2. This difference can be caused by different synthesis methods.

Table 2. The activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ based on the experimental results

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Activation Energies (eV)	References
0.48	Krok *et al*. [30]
0.52	Simner *et al*. [31]
0.20	Guillodo *et al*., [29]

The oxide ion MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increases with temperature rise (Figure 10~~8a~~). Based on the plot of ln (oxide ion diffusion coefficient) on I/T (Figure 10), the activation energy of the calculation result is 0.10 eV. Ion oxide MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increased with increase in temperature. Based on the plot of ln (oxide ion diffusion coefficient) versus I/T, the activation energy was 0.10 eV.

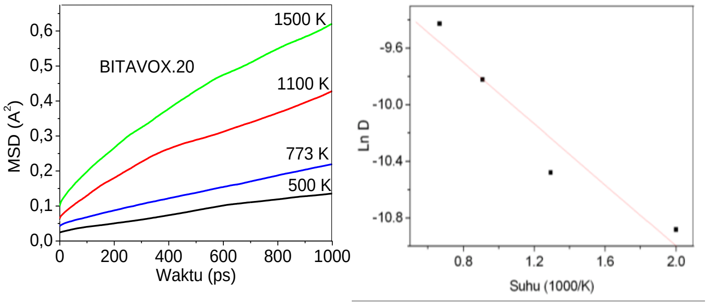

Figure 10~~8~~. Oxide ion MSD and ln D vs I/T plot of $Bi_2Ta_{0,2}V_{0,8}O_{5,5}$

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This activation energy was smaller than the activation energy calculated from *γ*-$Bi_2VO_{5.5}$ and $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$. This indicated that the conductivity of the $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ was greater than the conductivity of the two types of compound.

The addition of dopant partially to the parent compound (*γ*-$Bi_2VO_{5.5}$) gives rise to environmental irregularities in the vanadate layer which can inhibit oxygen migration. The irregularity is caused by different size of vanadium (V^{5+} = 0.54 Å) with dopants (Cu^{2+} = 0,73 Å; Ga^{3+} = 0,62 Å; Ta^{5+} = 0,64 Å) and increase of oxygen vacancy due to substitution of V^{5+} partially by Cu^{2+} and Ga^{3+}. On the contrary, doping with Ta^{5+} does not add vacancy because of Ta is isovalent with V. The vacancy can cause the strong attraction between vacancies and V/dopant thus increasing the activation energy of the migration of oxygen ion. The non-spherical *d* orbitals of Cu, with the configuration $3d^9$, also cause the vanadium environment to be distorted and can act as a trapping center in process of oxygen ion migration.

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Polarization of cations to oxygen ions can facilitate hopping of oxygen ion to vacancy site. This happens because the electron cloud of the oxide ion was pulled by the cation so that the oxide ion was easily moved from the site of the lattice. The polarization of the cations to the oxide ions that are getting stronger, will further facilitate the oxide ions to migrate in the crystal lattice. Ta^{5+} cations, theoretically, will be more strong at polarizing oxide ions compared to Ga^{3+} and Cu^{2+} cations, because Ta^{5+} has a greater charge density. As a result, qualitatively it can be predicted that at the same concentration, the increase of ionic conductivity is BICUVOX <BIGAVOX <BITAVOX.

CONCLUSIONS

Computational simulation of ionic conductivity of BIMEVOX and *γ*-$Bi_2VO_{5.5}$ performed using DFT, Mott-Littleton method, and molecular dynamic simualtion. The obtained enthalpy for *γ*-$Bi_2VO_{5.5}$ close to experimental results. Defect simulation using Mott-Littleton method showed 10% Cu^{2+}, 10% Ga^{3+}, and 20% Ta^{5+} where the highest ionic conductivity was in good agreement with the experiment results. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME= Cu and Ta close to experimental values. The addition of oxygen vacancy at *γ*-$Bi_2VO_{5.5}$ due to doping with aliovalent dopants, such as Cu and Ga, causes disordering polyhedral in the vanadate layer where oxygen ion migration takes place. In contrast, ordering polyhedral due to the inclusion of isovalent dopants such as Ta causes easier ion migration. To synthesize BIMEVOX compounds which are expected to have high ion conductivity, the concentrations of aliovalent and aliovalent dopants are 10% and 20%, respectively.

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Highest Ionic Conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational Modeling and Simulation

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Abstract: *BIMEVOX had the potential to play an important role in solid oxide fuel cell, especially as the electrolyte due to their high ionic conductivity. In this work, oxide ion migrations of γ-$Bi_2VO_{5.5}$ and BIMEVOX were simulated using density functional theory (DFT), Mott-Littleton method, and molecular dynamics simulation. In γ-$Bi_2VO_{5.5}$, there were oxygen vacancies at the equatorial position in the vanadate layers. These vacancies could facilitate oxide ions migration. The Enthalpy of the oxide migration for γ-$Bi_2VO_{5.5}$ based on DFT calculation was 0.38 eV, which was in good agreement with experimental results. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with Cu^{2+}, Ga^{3+}, and Ta^{5+}. Defect simulation results using the Mott-Littleton method showed that the total maximum energies of region II were achieved at concentrations of 10, 10, and 20%, respectively, for Cu^{2+}, Ga^{3+}, and Ta^{5+}. The calculated concentration of Cu^{2+}, Ga^{3+}, and Ta^{5+} was in good agreement with those of experiment results, where the highest ionic conductivity was obtained. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME = Cu and Ta) were 0.19, 0.21, and 0.10 eV, respectively, close to experimental values.*

Keywords: *simulation; vacancy defect; γ-$Bi_2VO_{5.5}$ and BIMEVOX; ionic migration*

■ INTRODUCTION

Solid electrolyte materials with high oxide ion conductivity intensively investigated in order to have a solid oxide fuel cell (SOFC). One of the oxide materials that had high oxide ion conductivity and the potential application was $Bi_2V_{1-x}Me_xO_{5.5-\sigma}$ (BIMEVOX), where ME was dopant [1-3]. Dopant at a certain concentration plays an important role in improving the ease of oxygen ions migration of $Bi_2VO_{5.5}$ [4-5]. Therefore, in addition to the migration path of oxygen ions, the search for a type of dopant with a certain concentration was needed to obtain BIMEVOX with high conductivity. The computational simulation method could be conducted first to predict the ease of ion migration.

BIMEVOX was a family of oxides derived from $Bi_2VO_{5.5}$ and obtained by doping into the vanadium site of $Bi_2VO_{5.5}$ by aliovalent or isovalent metal cations (ME). The structure of $Bi_2VO_{5.5}$ could be derived from Bi_2MoO_6 and δ-Bi_2MoO_6 by the formation of oxygen vacancies in the metal oxygen layers; thus, the compound can be formulated as $(Bi_2O_2)(VO_{3.5}\pi_{0.5})$, where π was corresponding to the intrinsic oxygen vacancies [6-7].

The $Bi_2VO_{5.5}$ goes to several structural transformations and known had several polymorphs, but essentially there were only three main polymorphs, namely α, β, and γ-$Bi_2VO_{5.5}$ with the transformations: α → β at 720 K and β → γ at 840 K. The structures of α and β-phases were more ordered, larger in unit cell and had lower conductivity. At the high temperature, γ-phase was formed and had a conductivity of 0.2 $\mathrm{Scm^{-1}}$ at 943 K [6]. The γ-$Bi_2VO_{5.5}$ can be stabilized by partial substitution of V^{5+} with other metal cations (ME) [8-9]. The substitution does not only stabilize the structure but also increases ionic conductivity due to the creation of vacancies [10-11]. Therefore, the computational simulation carried out in this study was the gamma phase of $Bi_2VO_{5.5}$ and BIMEVOX (ME = Cu^{2+}, Ga^{3+}, and Ta^{5+}).

The experimental results of BIMEVOX compounds showed the contribution of electrons that affected BIMEVOX conductivity [12]. Moreover, the texture of compounds, surface conditions, pore existence, and the presence of impurities affect ionic conductivity. A single phase of BITAVOX could not be obtained by synthesis [13]. Dereeper et al. reported that BITAVOX conductivity increases with the increase in Ta dopant concentration. BIGAVOX had a smaller conductivity due to the contribution of electron conductivity [13]. Therefore, the single phase of the gamma-$Bi_2VO_{5.5}$ and BIMEVOX (Cu^{2+}, $Ga^{3+,}$ and Ta^{5+}) through computational modeling and simulation was important to be conducted to predict the possibility of ease of migration of oxygen ions without the presence of electron conductivity.

Experimental studies on the oxide ionic conductivity of BIMEVOX have been reported elsewhere [14]. However, the experimental study could not reveal the detail of the mechanism of oxide ion conductivity and the role of dopant in the BIMEVOX on the structural properties. Computational studies could be used to study many material properties efficiently in order to save time and cost as well as to provide more detail mechanisms at the atomic level. Some computation study on the layered structure of Aurivillius phases similar to BIMEVOX has been carried out and reported [15-16]. It could reveal defect energies and maximum dopant concentrations in Aurivillius as ferroelectric material. From our best knowledge, the computational study on BIMEVOX was not reported yet.

Here, we report the computational study on BIMEVOX and its parent structure that cover the trajectory of ionic oxide in γ-$Bi_2VO_{5.5}$ and defect energy of BIMEVOX. The study was aimed to investigate the oxide ion pathways that were possible in the V^{5+} coordination environments of γ-$Bi_2VO_{5.5}$ as well as to predict dopant concentrations of Cu^{2+}, $Ga^{3+,}$ and Ta^{5+} that give the higher ionic conductivity. Subsequently, transport properties and activation energy of migration of oxygen ions of the parent compound and BIMEVOX (ME = $Cu^{2+}$and Ta^{5+}), which were predicted to have the highest ionic conductivity, were simulated using the molecular dynamics method. Those dopants were selected because of their ionic radius close to the ionic radius of V^{5+}. This means that the dopant with an ionic radius close to the V^{5+} radius could enhance the conductivity [17].

■ COMPUTATIONAL METHODS

Enthalpy of Oxide Ion Migration

The enthalpies of oxide ion migration of γ-$Bi_2VO_{5.5}$ were calculated by using a computational simulation method that is based on density functional theory (DFT). This simulation used the CASTEP code of Material Studio Modeling from Accerys, series number 3.2.00, in Politecnico di Torino [18]. The methodology for electronic structure calculations in CASTEP is as follows: set of one-electron Schrodinger (Kohn-Sham) equations are solved using the plane-wave pseudopotential approach. The wave functions are expanded in a plane wave basis set defined by the use of periodic boundary condition and Bloch's Theorem. The electron-ion potential is described by means of *ab initio* pseudopotentials within both norm-conserving and ultrasoft formulations. Direct energy minimization schemes are used to obtain self-consistently, the electronic wave functions and its corresponding charge density. Lattice optimization is initially performed using exchange–correlation energy functions of Perdew–Burke–Ernzerhof (GGA-PBE). Structural optimizations were implemented to determine the best functional approximation to perform in examining the enthalpy of γ-$Bi_2VO_{5.5}$ at various oxygen positions of the tetragonal vanadate layer. A k-point grid of 1×1×1 generated using the Monkhorst–Pack method for Brillouin zone sampling with an energy cut-off of 600 eV.

Atomistic simulation and Molecular Dynamic

The main samples used in this simulation were of two types, namely (i) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with an I4/mmm space group as reported by Mairesse et al. [17] and (ii) the tetragonal structure of γ-$Bi_2VO_{5.5}$ with P1 space group modified from the first structure. The two structures were then doped with a dopant (ME) of Cu, Ga, and Ta to obtain BIMEVOX compounds. In the first structure, the simulation method applied is atomistic simulation using GULP [19]. The simulation aims to calculate defect energy while predicting the ease of migration of oxygen ion in BIMEVOX based on the increase in dopant concentration. Meanwhile, the second structure applied molecular dynamics to determine the property of transport or activation energy of the migration of oxygen ions using the DLPOLY code [20]. Both simulation methods use Buckingham's short range potential defined:

$$\theta_{ij} = A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where A_{ij}, ρ_{ij} and C_{ij} were constant parameters, and r_{ij} was the distance between i and j ions. The first term in Eq. (1) describes short-range repulsion, while the second term shows induced dipole (van der Waals interaction).

Using DL_POLY, different defect concentrations were simulated by creating a supercell of 4×4×4 containing dopant concentrations (10% Cu and 20% Ta) and the respective amount of oxygen vacancies. The simulations were carried out for a step time of 0.0002 ps with an ensemble of constant temperature and volume (NVT) and algorithm of leapfrog that applied to the simulation box of 1088 ions.

Defect Energy of BIMEVOX

Calculation of energy defects in atomistic simulations is performed on the average structure of γ-$Bi_2VO_{5.5}$ and BIMEVOX with space group I4/mmm. The energy defect of BIMEVOX was calculated based on the Mott-Littleton method, which divides the crystal lattice into the two regions, namely regions I (inner sphere) and II (outer sphere). Region I is the spherical region surrounding defect, which is clearly in relaxation. Meanwhile, the region II is the outer spherical defect that has relatively weak force, which is interpreted with the quasi-continuum approximation method. In this way, the lattice relaxation can be modelled effectively, and also the crystal is not as a simple rigid lattice where the diffusion of ions occurs. If the force on the region II is small, it can be assumed that the response of ions in this region is pure harmonic. There are two kinds of defects, namely impurity, and vacancy defects. Impurity defect with a defect center of V^{5+} is substituted partially with dopants of Cu^{2+}, Ga^{3+}, and Ta^{5+}, while the defect of oxygen vacancies are intrinsic defect as well as its being created in equatorial position of oxygen, O(3). The concentration of dopants, which substitutes V partially, was compensated by a reduction of concentrations of oxygen, O(3), to neutralize the charge in BIMEVOX structure. Defect energy calculations were performed at concentrations of 5, 10, 15, and 20% for each dopant, except for Ta^{5+} that was also carried out at the concentration of 25 and 30%.

■ RESULTS AND DISCUSSION

Geometry optimization of the parent structure, γ-$Bi_2VO_{5.5}$, was an initial procedure to check the structure stability. The structure of γ-$Bi_2VO_{5.5}$ reported by Mairesse et al. [17], tetragonal, space group I4/mmm, cell unit dimension, a = 3.99176(4), b = 3.99176(4), and c = 15.4309(3) Å was used as a starting model. The mean V–O octahedron was encaged between eight Bi sites. However, due to the O(2) and O(3) split-sites, it was observed that there were several short O–O contacts; these preclude simultaneous occupation of many of these O sites, as shown in Fig. 1.

In fact, the V–O environment, which appears as an octahedron squashed along the c stacking direction, must be viewed as the result of a superimposed polyhedral. Indeed, by selecting appropriate O sites among those drawn, the classical O environments of the V cation are easily recognized as octahedron, tetrahedron, trigonal bipyramid, and tetragonal pyramid with interatomic distances compatible with O atomic size [10]. Therefore, the structure, that has high symmetry and contains oxygen vacancy, can be represented using by space group P1 that had no symmetry, as shown in Fig. 2.

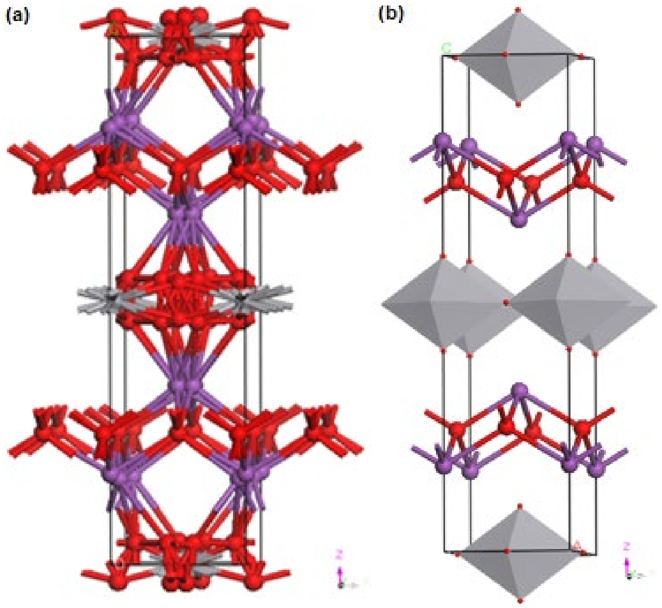

Fig 1. The crystal structures of $Bi_2VO_{5.5}$, (a) average crystallography structure, and (b) the refined structure oxygen vacancies were shown as oxygen atoms

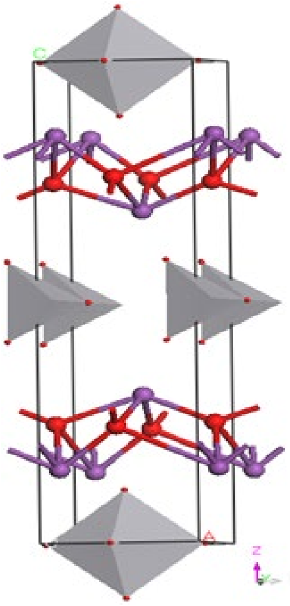

Fig 2. The one possibility of a structure that has V - O tetrahedral environment with oxygen vacancy in the equatorial site

The structure in Fig. 2 was one of the models of structure γ-$Bi_2VO_{5.5}$, showing a special vanadium-oxygen anions coordination environment. The structure that is simulated based on DFT indicates that the coordination environment of V cations by O(3) and oxygen vacancy are in good agreement with the crystallography site of γ-$Bi_2VO_{5.5}$ structure, as depicted in Fig. 1(a) and 2. Therefore, the crystal structure (Fig. 2) can be used as a starting structure to determine activation energy that represents oxygen jump and the easiness of ionic conduction.

Pathway of Oxide Ion Migration of $Bi_2VO_{5.5}$

Oxygen ions, which surround the vanadium ions (Fig. 3), could be divided into two types, namely apical site, O(2), and equatorial site, O(3). Geometry optimization results of a γ-$Bi_2VO_{5.5}$ show that the angle that occupied O(3)-V-vacant O(3) against V was 70 degrees, with O(3)-V bond length of 1.72 Å. Throughout this 70 degrees angle, all the different positions of O(3) are optimized to describe oxygen pathways in the equatorial site as shown in Fig. 3.

Based on the result of the optimized geometry of γ-$Bi_2VO_{5.5}$, the enthalpies of O(3) migration were calculated. The O(3) was moved from one position to the other vacant position. The oxygen position with the highest energy, is in the middle between occupied position (initial position) and vacant position, as shown in Fig. 4.

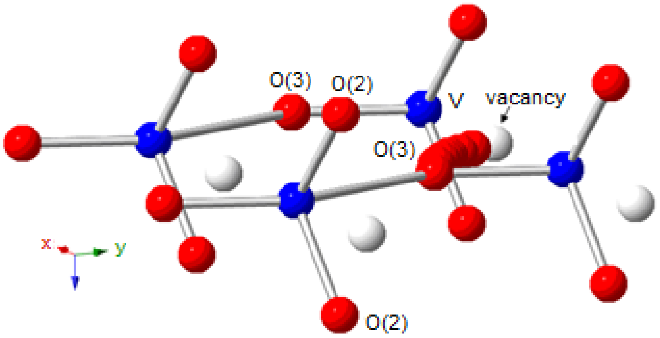

Fig 3. V coordination environments by oxide ions, O(3) equatorial oxygens and O(2) apical oxygens

The calculated activation energy of oxygen pathway was 0.38 eV and is in good agreement with experiment results, as given in Table 1.

Defect Energy of BIMEVOX

The calculation of defect energy was an important step to treat the lattice relaxation of point defect or migrating ion. In this study, the defect energy of BIMEVOX was calculated based on Mott-Littleton method. The number of ions involved in this defect energy

Table 1. Activation energies (eV) of oxygen ion motion in γ-$Bi_2VO_{5.5}$ based on this simulation work and these obtained from experiment work

Calculation (this work	Experiment [ref.]	Description
0.384	0.3427 [14]	The temperature of 773 K, the sample obtained from a solid state reaction at sintering temperature of 1073 K for 10 and 12 h
	0.35 [15]	The temperature of 873 K, the sample obtained from a solid state reaction at a sintering temperature of 1113 K for 5 h
	0.4 [21]	High temperature, the sample obtained from solid state reaction at sintering temperature of 1103 k for 24 h

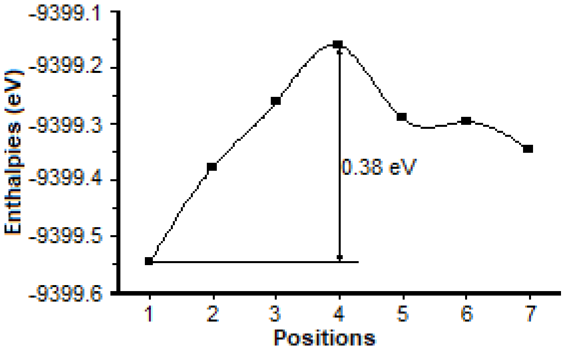

Fig 4. Enthalpies of oxygen migration as a function of the vacancy position in the γ-$Bi_2VO_{5.5}$ structure

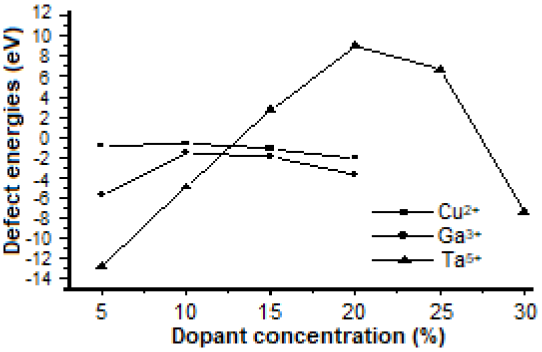

Fig 5. Energy defect in region II as a function of dopant concentration. BIMEVOX structure was expected to more conductive at a dopant concentration of 10% Cu, 15% Ga, and 20% Ta

calculations was 5,604 ions for the region I and 103,016 ions for region II, with each radius was and 37 Å, respectively. The defect energy calculation results were summarized in Fig. 5.

The results of the defect energy calculations show that the defect energy values of region II vary according to the dopant type and concentration. Energy defect increases up to concentration of 10% for all dopants. However, for Ta^{5+}, defect energy increases with the concentration of up to 20%. This was as expected because of Ta is isovalence to V, with valence = +5. Maximum defect energy values were reached at concentrations of 10% for Cu and Ga, and 20% for Ta, with values of -0.63, -1.57 and 8.98 eV, respectively. BICUVOX and BIGAVOX defect energies are more negative at a concentration of more than 10%, and the BITAVOX defect energies have the highest negative values at concentrations of 5 and 30% Ta. The negative values of defect energy show that the response of ion is pure harmonic and unstable. However, the BIMEVOXes can be synthesized at the concentrations.

Oxygen vacancies can be varied in accordance with the dopant valence and concentration. The dopant concentration increases the amount of oxygen vacancies in positions O(3). The preference of dopants affects symmetry and connectivity of polyhedral in the perovskite-like layer. Consequently, the performance of ionic conductivity is also expected to significantly depend on the defect structure and the effect of trapping on the diffusion pathway of oxygen [14]. Therefore, a stable structure is achieved when each dopant is at a certain concentration. Based on the defect energy values in this work, the concentration of dopants that stabilized γ-$Bi_2VO_{5.5}$ and were predicted to have the highest conductivity are 10% for Cu, 10% for Ga, and 20% for Ta. At these concentrations, the cation polarizability of dopants is predicted to have achieved maximum value so that it facilitates the oxide ion diffusion process in the like-perovskite layers. Again, we predict that sequences of decreasing conductivity of BICUVOX, BIGAVOX, and BITAVOX are 10>15>20% for Cu; 10>15>20% for

Ga; and 20>25>15>30% for Ta, respectively, as Fig. 5. These are in agreement with the experimental results reported by Kant et al., Lazure et al., and Murasheva et al. [22-24]. At concentrations of more than 10% Cu, the ionic conductivity of BICUVOX decreases with the increasing vacancy because in its like-perovskite volume increase.

Concentration value of 10% Cu in this study is in good agreement with experimental results reported by Kant et al. [22] which showed the stable structure of BICUVOX at 10%, which has a grain pattern and uniform in size with adequate porosity, compared to the concentrations of 15 and 20%. Concentration of 20% Ta also in good agreement with the experimental results reported by Lazure et al., which states that the best conductivity for BITAVOX achieved at a concentration of 20% Ta [23]. BIGAVOX has also the highest conductivity at a concentration of 10% Ga for the gamma phase. According to Kant et al., BIGAVOX has the highest conductivity at 10% for a beta phase, not the gamma phase [12]. While according to Murasheva et al. BIGAVOX phase was gamma at 10% Ga with more uniform grain [24].

Property of Transport and Activation Energy of BIMEVOX

Molecular dynamics simulations of $Bi_2VO_{5.5}$ starting with geometry optimization of the supercell (4×4×4) of $Bi_2VO_{5.5}$ using DLPOLY. In the perovskite layers of the supercell $Bi_2VO_{5.5}$, coordinations of V–O were 4 and 6 that arranged alternately between the bismuth layers (Fig. 6(a)). Coordination 4 of V–O (Fig. 6(c)) is square planar, and the coordination 6 is regular octahedral (Fig. 6). Since the superstructure is optimized, the ions were distorted in layers of bismuth and perovskite layer as shown in Fig. 6(d). The square planar of V–O turn

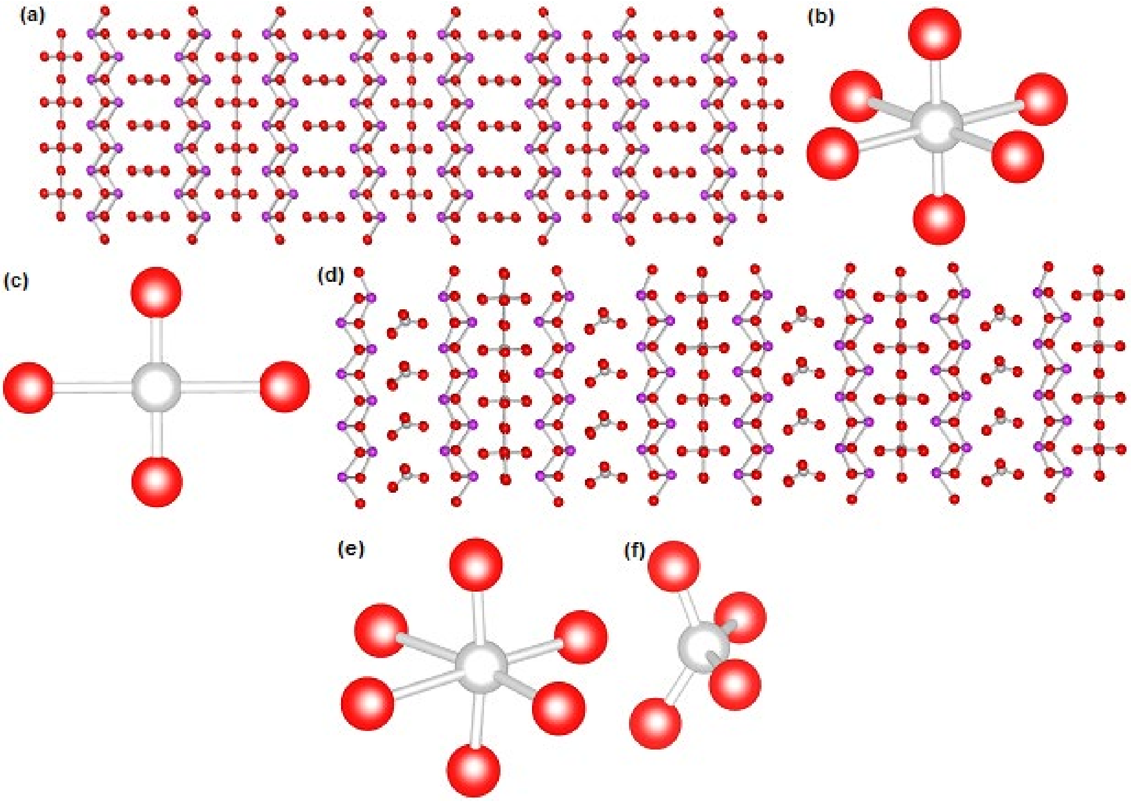

Fig 6. Super cell structure (4×4×4) $Bi_2VO_{5.5}$: (a) before optimization and (d) after optimization using DLPOLY code. In the perovskite-like layer, flat rectangular coordination (c) of the V–O has been changed into tetrahedral coordination (f), and the regular octahedral coordination (b) experienced distorted octahedral coordination (e). In an optimized structure, the ions in the bismuth layer are also distorted

into tetrahedral coordination (Fig. 6(f)), and the octahedral coordination is distorted (Fig. 6(e)). Therefore, the results of the supercell optimization of $Bi_2VO_{5.5}$ in accordance with the expected structure, which is also very similar to the results of the optimization of the unit cell $Bi_2VO_{5.5}$ using the DFT method.

The successful optimization of the $Bi_2VO_{5.5}$ supercell using DLPOLY has proven that this works well, and the short range potential of Buckingham between ions was also correct. Therefore, DLPOLY can be used to perform geometry optimization and molecular dynamics simulations of $Bi_2VO_{5.5}$. Furthermore, the transport properties (through molecular dynamics simulations) of $Bi_2VO_{5.5}$ studied by creating a supercell structure with VO coordinations were coordination mixtures of tetrahedral, coordination five, and octahedral. The coordination mixtures were representative to show the transport properties of the $Bi_2VO_{5.5}$ compound.

Molecular dynamics (MD) simulation were carried out on γ-$Bi_2VO_{5.5}$ and BIMEVOX that were predicted the easiest migration of oxygen ions as atomistic simulation results above, namely $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$, $Bi_2Ga_{0.1}V_{0.9}O_{5.4}$, and $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$. Before the MD simulation, the supercells of γ-$Bi_2VO_{5.5}$ and BIMEVOX were optimized first. The optimized structure was controlled at several temperatures to determine the properties of ion transport, such as mean square displacement (MSD) and activation energy. MSD was defined by the formula:

$$MSD_{\beta}(t)=\frac{1}{N}\sum_{i=1}^{N}\left[r_i(t)-r_i(0)\right]^2 \qquad (2)$$

where $r_i(t)$ was the position of ion i at time t. In a perfect lattice, the MSD of component ions usually ranges from the average value. Meanwhile, in the defect lattice, there were mobile ions, such as O^{2-} in γ-$Bi_2VO_{5.5}$, where MSD increases over time. Fig. 7 shows the MSD data of the γ-$Bi_2VO_{5.5}$ plotted as a function of time at temperatures of 500, 700 and 1100 K. This shown that there were migrating oxide ions, where the temperature rise was followed by an increase in the diffusion of oxide ion.

From the plot of slope MSD can be determined by the diffusion coefficient (D_{β}) using correlation:

$$MSD_{\beta}(t)=6D_{\beta}(t)-MSD_{\beta}(0) \qquad (3)$$

where $MSD_{\beta}(0)$ was an atomic vibration factor arising from ion vibrations. The calculation of the diffusion coefficient at the three temperatures specified in Fig. 8. The calculation can be evaluated for the activation of ion migration using the Arrhenius relationship.

Based on the Arrhenius plot (ln D vs. 1/T) above, the activation energy obtained is 0.19 eV. This value was a value commonly found in experiments, as reported by Joubert et al. [25].

MSD of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ increases with increasing temperature as shown in Fig. 9. This indicated that the diffusion of oxide ions increases with increasing temperature. At a temperature of 500, 773 and 823 K, the MSD plot rises to a straight line compared to the MSD plot

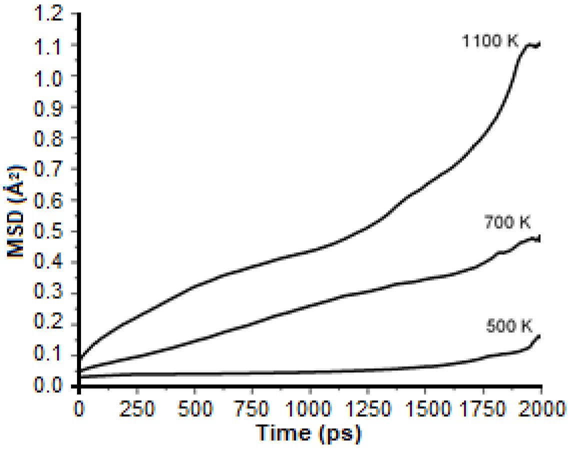

Fig 7. MSD of the oxide ions of γ-$Bi_2VO_{5.5}$ at temperatures of 500, 700, and 1100 K. The MSD receives an increase in temperature, which indicates that the diffusion of oxide ions also increases

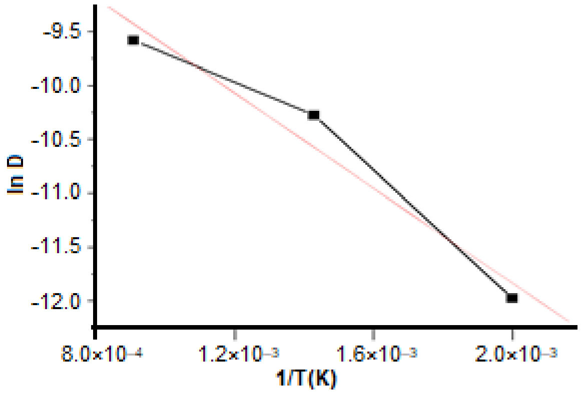

Fig 8. Plot ln D vs. 1/T for oxide ions of γ-$Bi_2VO_{5.5}$

at 873 K. At 873 K, the oxide ion migration rises rapidly to the timestep 160 ps, then the migration rises slowly to 480 ps, as shown in MSD with lines that are not straight (curved). At the timestep 160–480 ps, the migration of oxide ions was estimated to pass through the obstruction area. This kind of thing is observed in the migration of sodium ions of zeolites [26].

The diffusion coefficient of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ at some temperatures was shown in Fig. 9. Based on this graph, the ion activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ was 0.21 eV. This energy value was in accordance with the results of experiments reported by Guillodo et al. [27], but different from those reported by Krok et al. [28] and Simner et al. [29] as shown in Table 2. This difference can be caused by different synthesis methods.

The oxide ion MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increases with temperature rise (Fig. 10). Based on the plot of ln (oxide ion diffusion coefficient) on I/T (Fig. 10), the activation energy of the calculation result is 0.10 eV. Ion oxide MSD of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ also increased with an increase in temperature. Based on the plot of ln (oxide ion diffusion coefficient) versus I/T, the activation energy was 0.10 eV.

This activation energy was smaller than the activation energy calculated from γ-$Bi_2VO_{5.5}$ and $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$. This indicated that the conductivity of the $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ was greater than the conductivity of the two types of compounds.

The addition of dopant partially to the parent compound (γ-$Bi_2VO_{5.5}$) gives rise to environmental irregularities in the vanadate layer, which can inhibit oxygen migration. The irregularity is caused by different size of vanadium (V^{5+} = 0.54 Å) with dopants (Cu^{2+} = 0.73 Å; Ga^{3+} = 0.62 Å; Ta^{5+} = 0.64 Å) and increase of oxygen vacancy due to substitution of V^{5+} partially by Cu^{2+}

Table 2. The activation energy of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ based on the experimental results

Activation Energies (eV)	References
0.48	Krok et al. [28]
0.52	Simner et al. [29]
0.20	Guillodo et al. [27]

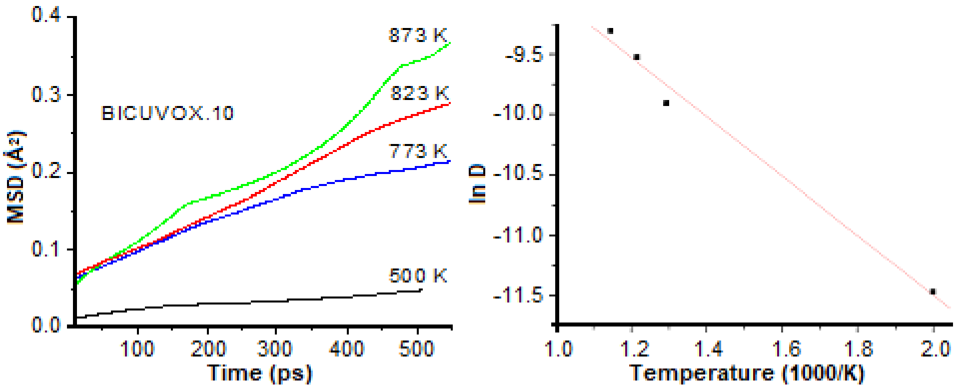

Fig 9. MSD and Plot of ln D vs. 1/T of oxide ion of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$

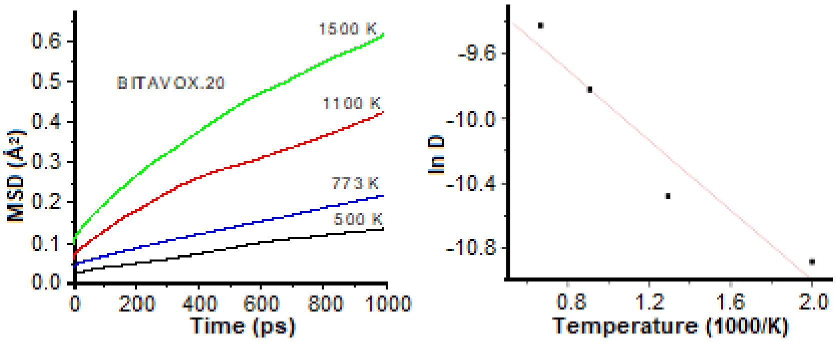

Fig 10. Oxide ion MSD and ln D vs. I/T plot of $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$

and Ga^{3+}. On the contrary, doping with Ta^{5+} does not add a vacancy because of Ta is isovalent with V.

The vacancy can cause a strong attraction between vacancies and V/dopants, thus increasing the activation energy of the migration of oxygen ion. The non-spherical d orbitals of Cu, with the configuration $3d^9$, also cause the vanadium environment to be distorted and can act as a trapping center in the process of oxygen ion migration.

Polarization of cations to oxygen ions can facilitate the hopping of oxygen ion to the vacancy site. This happens because the electron cloud of the oxide ion was pulled by the cation so that the oxide ion was easily moved from the site of the lattice. The polarization of the cations to the oxide ions that are getting stronger will further facilitate the oxide ions to migrate in the crystal lattice. Ta^{5+} cations, theoretically, will be stronger at polarizing oxide ions compared to Ga^{3+} and Cu^{2+} cations, because Ta^{5+} has a greater charge density. As a result, qualitatively it can be predicted that at the same concentration, the increase of ionic conductivity is BICUVOX<BIGAVOX< BITAVOX.

■ CONCLUSION

Computational simulation of ionic conductivity of BIMEVOX and γ-$Bi_2VO_{5.5}$ performed using DFT, Mott-Littleton method, and molecular dynamics simulation. The obtained enthalpy for γ-$Bi_2VO_{5.5}$ close to experimental results. Defect simulation using the Mott-Littleton method showed 10% Cu^{2+}, 10% Ga^{3+}, and 20% $Ta^{5+,}$ where the highest ionic conductivity was in good agreement with the experiment results. The results of the molecular dynamics simulation showed that the activation energies of oxide ion migration in γ-$Bi_2VO_{5.5}$ and BIMEVOX (ME = Cu and Ta close to experimental values. The addition of oxygen vacancy at γ-$Bi_2VO_{5.5}$ due to doping with aliovalent dopants, such as Cu and Ga, causes disordering polyhedral in the vanadate layer where oxygen ion migration takes place. In contrast, ordering polyhedral due to the inclusion of isovalent dopants such as Ta causes easier ion migration. To synthesize BIMEVOX compounds that are expected to have high ion conductivity, the concentrations of aliovalent and aliovalent dopants are 10% and 20%, respectively.

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